PB85-116192

Evaluation of an ESCA (Electron Spectroscopy for Chemical Analysis)/Leachate Analytical Scheme to Characterize Process Stream Wastes

GCA Corp., Bedford, MA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Oct 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-116192

EPA-600/2-84-156
October 1984

EVALUATION OF AN ESCA/LEACHATE ANALYTICAL SCHEME TO CHARACTERIZE PROCESS STREAM WASTES

by

Barbara M. Myatt

GCA CORPORATION
GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts 01730

Contract No. 68-02-3129
Technical Directive No. 119

Project Officer

Frank E. Briden
Process Measurements Branch
Industrial Environmental Research Laboratory
Research Triangle Park, N.C. 27711

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-84-156

2.

3. RECIPIENT'S ACCESSION NO. PB8 5 116192

4. TITLE AND SUBTITLE Evaluation of an ESCA/Leachate Analytical Scheme to Characterize Process Stream Wastes

5. REPORT DATE October 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) Barbara M. Myatt

8. PERFORMING ORGANIZATION REPORT NO. GCA-TR-83-92-G

9. PERFORMING ORGANIZATION NAME AND ADDRESS
GCA/Technology Division
213 Burlington Road
Bedford, Massachusetts 01730

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO. 68-02-3129, Task 119

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED Task Final; 4-9/82

14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Frank E. Briden, Mail Drop 62, 919/541-7808.

16. ABSTRACT

The report gives results of an evaluation of the ability of an ESCA/leachate analytical scheme to characterize solid waste from combustion processes and hazardous waste incinerators. Samples were analyzed for surface elemental composition by electron spectroscopy for chemical analysis (ESCA) before and after aqueous leaching. Selected elements were subjected to oxidation state studies by ESCA, and leachates were analyzed for anions by ion chromatography and for trace metals by inductively coupled plasma spectrometry. The results of ESCA before and after leaching compared favorably with leachate data. Although aqueous leaching did not significantly affect the metal species present in the samples used in this study, it did extract considerable amounts of water-soluble ions: sodium, calcium, chloride, and sulfate. Essentially all samples showed an increase in oxygen after leaching that was attributed to hydration by the aqueous extraction medium. ESCA can successfully speciate chromium, lead, and zinc when these elements are sufficiently abundant in the sample. The technique is limited, however, by its ability to detect only those elements present at > 0.1 to 1.0 % atomic. Most process wastes contain very low concentrations of metals, thereby minimizing the suitability of ESCA for process waste characterization.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Waste Treatment	Pollution Control	13B	
Chemical Analysis	Toxicity	Stationary Sources	07D	06T
Spectroscopy	Leaching	ESCA	14B	07A
Electronic Spectra	Particles	Hazardous Waste		14G
Incinerators	Chromatography	Particulate		
Combustion	Spectroscopy	Ion Chromatography	21B	

18. DISTRIBUTION STATEMENT Release to Public

19. SECURITY CLASS *(This Report)* Unclassified

20. SECURITY CLASS *(This page)* Unclassified

21. NO. OF PAGES 138

22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

An ESCA/leachate analytical scheme was evaluated for its ability to characterize solid waste from combustion processes and hazardous waste incinerators. Samples were analyzed for surface elemental composition by ESCA before and after aqueous leaching. Selected elements were subjected to oxidation state studies by ESCA, and leachates were analyzed for anions by ion chromatography and for trace metals by inductively coupled plasma spectrometry. The results of ESCA before and after leaching compared favorably with leachate data. Although the aqueous leaching procedure did not significantly affect the metal species present in the samples used in this study, it did extract considerable amounts of water-soluble ions: sodium, calcium, chloride, sulfate. Essentially all samples showed an increase in oxygen after leaching that was attributed to hydration by the aqueous extraction medium.

ESCA can successfully speciate chromium, lead, and zinc when these elements are sufficiently abundant in the sample. The technique is limited, however, by its ability to detect only those elements present at greater than 0.1 to 1.0 percent atomic. Most process wastes contain very low concentrations of metals, thereby minimizing the suitability ESCA for process waste characterization. However, municipal and hazardous waste incinerators produce bottom and baghouse ashes containing significant amounts of hazardous trace metals. ESCA in conjunction with process data, could prove useful in determining metal species present and their potential for release from particulate.

CONTENTS

Abstract iii
Figures vi
Tables vii
Acknowledgment x

1. Introduction 1
2. Conclusions and Recommendations 2
    Conclusions 2
    Recommendations 3
3. Background and Scope of Work 4
    The ESCA Analytical Technique 4
    Scope of Work 6
4. Quality Assurance Program 9
    Internal Quality Control Checks 9
    Precision, Accuracy and Completeness 9
    Performance Audits 11
    System Audits 11
    Quality Problems and Corrective Actions 11
5. Experimental Program 12
    Acquisition of Samples 12
    Leachate Generation 14
    ESCA Analysis of Solid Samples 16
    Electron Spectroscopy for Chemical Analysis 16
    Chemical Analysis of Leachates 17
    Data Reduction 19
6. Results and Discussions 22
    Elemental Analyses by ESCA 22
    Metals Speciation by ESCA 42
    Analysis of Leachate Solutions 51
    ESCA Before and After Leaching 58

References 66

Appendices

A. QA Audit 68
B. Broadband Spectra for Elemental Quantification 72

Preceding page blank

FIGURES

Number		Page
1	Broadband ESCA spectrum of sludge incinerator particulate . . .	5
2	Broadband ESCA spectrum of a hi vol filter	18
3	Stainless steel substrate blank	34
4	Sticky tape substrate blank	35
5	Speciation of chromium by ESCA	45

TABLES

Number		Page
1	Precision Data Tables	10
2	Summary of Samples Obtained and Number of Aliquots Leached and Analyzed by ESCA	13
3	Selected Scan Parameters for ESCA Analysis	16
4	Operating Parameters for IC	19
5	Selected Elemental Sensitivity Factors (F) for the ESCA-36	20
6	ESCA Results (Percent Atomic): Sample 3610, Before Leaching	23
7	ESCA Results (Percent Atomic): Sample 9949, Before Leaching	23
8	ESCA Results (Percent Atomic): Sample 24616, Before Leaching	24
9	ESCA Results (Percent Atomic): Sample 24616, Before Leaching	24
10	ESCA Results (Percent Atomic): Sample 1633a, Before Leaching	25
11	ESCA Results (Percent Atomic): Sample 029-QC-1, Before Leaching	25
12	ESCA Results (Percent Atomic): Sample 029-QC-2, Before Leaching	26
13	ESCA Results (Percent Atomic): Sample 27745, Before Leaching	26
14	ESCA Results (Percent Atomic): Sample 27746, Before Leaching	27
15	ESCA Results (Percent Atomic): Sample 27747, Before Leaching	27
16	ESCA Results (Percent by Weight): Sample 27747, Before Leaching	28
17	ESCA Results (Percent Atomic): Sample 27748, Before Leaching	28

TABLES (continued)

Number Page

18 ESCA Results (Percent Atomic): Sample 29174, Before Leaching . 29

19 ESCA Results (Percent Atomic): Sample 3610, After Leaching . . 30

20 ESCA Results (Percent Atomic): Sample 9949, After Leaching . . 30

21 ESCA Results (Percent Atomic): Sample 24616, After Leaching. . 31

22 ESCA Results (Percent Atomic): Sample 27745, After Leaching . 31

23 ESCA Results (Percent Atomic): Sample 27746, After Leaching . 32

24 ESCA Results (Percent Atomic): Sample 29174, After Leaching . 32

25 Effect of Substrate on Concentrations Results by ESCA 36

26 Evaluation of Blind Duplicates by ESCA (Percent Atomic) 38

27 Evaluation of Blind Duplicates by ESCA (Percent Atomic) 39

28 Evaluation of Blind Duplicates by ESCA (Percent Atomic) 40

29 Comparison of Measured Concentrations for NS=5 Scans and NS=10 Scans 43

30 Energy Shifts of Chromium Standards 44

31 Lead Speciation of Standard Compound 47

32 Comparison of Experimental and Literature Values for Lead Speciation 49

33 Lead Speciation in Incinerator Particulates 50

34 Zinc Speciation of Standard Compounds 50

35 Zinc Speciation in Incinerator Particulate 51

36 IC Results (μg/ml) of Leachate Analysis (Sample 3610) 52

37 IC Results (μg/ml) of Leachate Analysis (Sample 9949) 52

38 IC Results (μg/ml) of Leachate Analysis (Sample 24616) 52

39 IC Results (μg/ml) of Leachate Analysis (Sample 029-QC-1, Blind Duplicate of Sample 3610) 53

TABLES (continued)

Number Page

40 IC Results (μg/ml) of Leachate Analysis (Sample 029-QC-2, Blind Duplicate of Sample 24616) 53

41 IC Results (μg/ml) of Leachate Analysis (Sample 27745) 53

42 IC Results (μg/ml) of Leachate Analysis (Sample 27746) 54

43 IC Results (μg/ml) of Leachate Analysis (Sample 29174) 54

44 ICP Results (μg/ml) of Leachate Analysis (Sample 3610) 55

45 ICP Results (μg/ml) of Leachate Analysis (Sample 9949) 55

46 ICP Results (μg/ml) of Leachate Analysis (Sample 24616) 55

47 ICP Results (μg/ml) of Leachate Analysis (Sample SRM 1633a) . . 56

48 ICP Results (μg/ml) of Leachate Analysis (Sample 029-QC-1, Blind Duplicate of Sample 3610) 56

49 ICP Results (μg/ml) of Leachate Analysis (Sample 029-QC-2, Blind Duplicate of Sample 24616) 56

50 Comparison of Elemental Composition Before and After Leaching (Sample 3610) 59

51 Comparison of Elemental Composition Before and After Leaching (Sample 9949) 59

52 Comparison of Elemental Composition Before and After Leaching (Sample 24616) 60

53 Comparison of Elemental Composition Before and After Leaching (Sample 27745) 61

54 Comparison of Elemental Composition Before and After Leaching (Sample 27746) 62

55 Comparison of Elemental Composition Before and After Leaching (Sample 27746) 63

56 Comparison of Elemental Composition Before and After Leaching (Sample 29174) 64

ACKNOWLEDGMENT

The author would like to acknowledge the support and assistance provided by the EPA Project Officer, Frank Briden, and the GCA Project Managers, Kenneth T. McGregor and David Stern. I would also like to thank Greg Jungclaus and James Spigarelli of the Midwest Research Institute for providing many of the samples used in this study.

SECTION 1

INTRODUCTION

Solid waste from refuse incineration presents a landfill disposal problem owing to its potentially hazardous nature. Significant leaching from fly ash and bottom ash has been shown to occur when these materials are exposed to neutral or slightly acidic solutions simulating rainwater. In a landfill disposal situation, ground water quality would be affected by the amounts and types of compounds thus leached.

Incinerator residue leachates and acid digestions have been characterized for anion and cation content but the actual solid waste has not been studied before and after leaching to determine changes in its composition. Electron spectroscopy for chemical analysis (ESCA or XPS) is a surface analysis technique and was expected to be useful for obtaining such information. With ESCA, only the top 20 to 100 Å of the solid or particulate surface are analyzed, and in leaching studies, it is this part of the sample that is of interest. ESCA provides elemental composition data for all elements except hydrogen and helium. In addition, for a number of elements, ESCA can be used to determine oxidation state and bonding information.

This project was designed to evaluate a combined ESCA/leachate analytical scheme for characterizing the leachability of wastes from process streams. ESCA was used to analyze waste samples (fly ash, bottom ash) before and after leaching, and to provide an estimate of oxidation state (speciation) for several elements. Chemical analyses of the leachates were used to provide supporting data for the ESCA/leachate results.

Section 2 provides a summary of conclusions and recommendations based on the data. Section 3 describes the ESCA analytical technique and details the scope of work of this study. Section 4 contains a description of the Quality Assurance Program, and Section 5 includes the Experimental Program conducted. Section 6 presents experimental and QA/QC results and discusses the data in regard to the goals of the program. Appendix A contains the QA Audit Report and Appendix B contains ESCA Spectra for Elemental Quantification of Samples.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The experimental program for evaluating the utility of an ESCA/leachate analytical scheme consisted of replicate analyses of actual source particulate samples using ESCA, Level 1 aqueous leachate generation, ion chromatography, and inductively coupled plasma emission spectroscopy. Details of the experimental approach are given in Section 5 and the complete results are discussed in Section 6. The statements presented here serve to highlight the conclusions and recommendations reached from an examination of the data.

CONCLUSIONS

The following conclusions have been made from the data obtained in this study:

- Elemental identifications by ESCA are reproducible for major components (>5 percent atomic), but minor elements are often misidentified as noise or vice-versa.

- Quantification by ESCA is fairly precise (15 percent RSD) for most elements present as major components or for which ESCA has high sensitivity. This precision holds only for homogeneous samples or samples for which representative aliquots can be mounted on ESCA substrates. Elements producing low photoelectron counts show much greater variation in quantification which is attributable to subjective decisions by the analyst.

- The material used as substrates to mount samples in the ESCA appears to introduce no consistent bias in the concentrations of elements measured in the samples.

- The Level 1 aqueous leaching procedure has a rather low extraction efficiency for many species found in process waste samples. It too suffers from poor precision when inhomogeneous samples or nonrepresentative aliquots are analyzed.

- ESCA can be used to speciate chromium, lead and zinc when these elements are present in fairly high concentrations. At the detection limit, they do not produce sharp enough peaks for the analyst to determine a precise binding energy for the element. As learned through previous ESCA work, it is also possible to speciate sulfur and carbon in samples of this type.

- The ESCA/leachate analytical scheme can be used to detect changes in sample composition caused by aqueous leaching. As expected, water soluble components are easily extracted from the sample while metals show an apparent increase in concentration after leaching. This is primarily due to the removal of the soluble surface components. The species of metals present in the samples did not seem to change after leaching.

RECOMMENDATIONS

The following recommendations are based on the results of this experimental program:

- The combined ESCA/leachate analytical scheme should not be pursued as a means for determining the degree of hazard associated with disposal of process wastes. The combined procedure requires a great deal of analytical time and the benefits of post-leaching ESCA analyses appear minimal based on the samples used in this study. Although other samples may behave differently, it must be recognized that these samples (containing metals at concentrations detectable by ESCA) were extremely difficult to obtain and will probably not be routinely encountered in practice.

- The use of ESCA alone to predict aqueous leachability should be considered. Its focussing on the surface of particulate matter and its ability to detect elements and species of high aqueous solubility recommend it for this purpose. This statement is based on the supposition that, under the conditions of the Level 1 leaching procedure, only small amounts of trace metals will be leachable from the waste. This statement is supported by the literature.

- The use of ESCA to determine trace metal oxidation states could prove useful in a study attempting to correlate the metal compounds formed during incineration with combustion conditions and the type of waste. Similar work has already been performed using metal compound volatility as a predictor of whether the metal will accumulate in flyash, bottom ash, scrubber slurry, or will be emitted from the stack. Adding the speciation capabilities of ESCA to this evaluation could prove quite interesting.

SECTION 3

BACKGROUND AND SCOPE OF WORK

The surface analysis technique of ESCA has been suggested as a means of determining the leachability of potentially hazardous wastes. This program was conducted to evaluate the capabilities and applicability of ESCA to this purpose, but prior to presenting the study and its results in detail, it is appropriate to briefly describe the ESCA technique and outline the project scope of work.

THE ESCA ANALYTICAL TECHNIQUE

Electron spectroscopy for chemical analysis (ESCA), also known as x-ray photoelectron spectroscopy (XPS), is a surface elemental analysis technique capable of detecting all elements except hydrogen and helium. In ESCA, a constant energy x-ray beam, usually MgKα at 1253.6 eV or AlKα at 1486.6 eV, impinges on a surface inducing core (nonvalence) electrons to be ejected with discrete kinetic energies. These energies are determined by the energy of the x-ray source (E_{x-ray}), the work function of the spectrometer (W), and the characteristic binding energy (E_B) of the electron. Binding energy is defined as the energy required to remove a given electron from an atom of a particular element. The energy relationship can be expressed by the following equation:

$$E_B = E_{x-ray} - E_K - W$$

The x-ray energy and machine work function are constant for any given analysis; therefore, the binding energy can be calculated from kinetic energy.

Most ESCA instruments are designed to separate the different photoelectrons by filtering them according to their kinetic energies and generally produce data already calculated as binding energy. ESCA data take the form of spectra in which binding energy forms the x-axis and intensity in electron counts per second forms the y-axis. A typical broadband scan from analysis of particulate matter is shown in Figure 1. Peaks in the electron energy spectrum can be identified by comparison with tabulated data of electron binding energies.[1] Generally, the primary (or strongest) photoelectrons are sufficient to identify the precursor elements in the sample. However, secondary electrons may be needed to provide support for more difficult identifications.

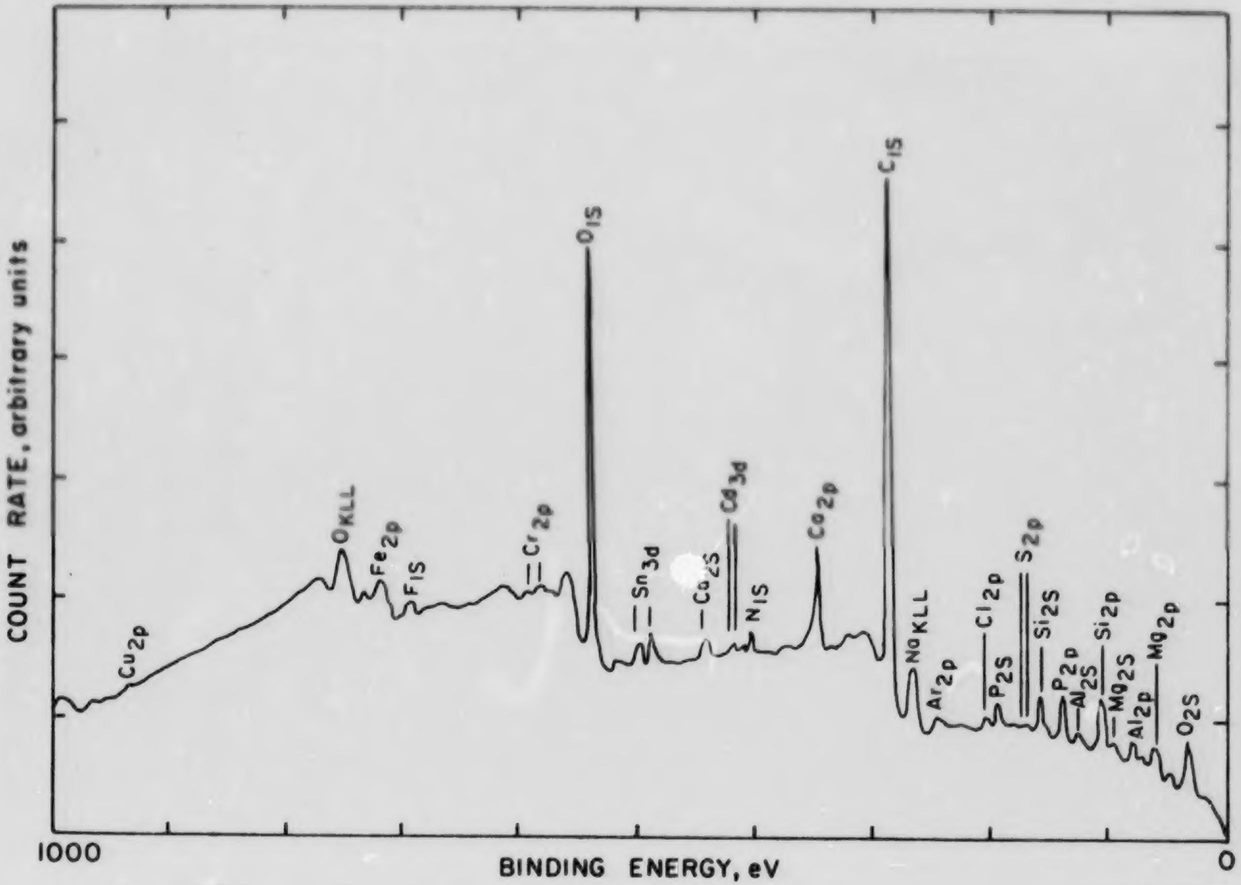


Figure 1. Broadband ESCA spectrum of sludge incinerator particulate.

Quantification is accomplished by measuring the peak height of the most intense line of each element, dividing the intensity of each line by its sensitivity factor, and normalizing each value to the total surface response. Data are reported as percent atomic and may also be calculated as percent by weight. Relative sensitivities for most electrons have been calculated and/or empirically determined and are available in the literature.[2] As necessary, these published values may be translated to terms compatible with different types of energy analyzers. The formulas and sensitivity factors used in this program can be found in Section 5.

In addition to the determination of elemental composition, ESCA is capable of distinguishing between different oxidation states and compound forms of some elements. Because the binding energy of an electron is influenced by its charge and its electrostatic environment, different ions of the same element will have slightly different binding energies for the same electron. In some elements this binding energy shift is on the order of the instrument resolution and is thus difficult to detect. However, other elements display substantially greater shifts of 1 eV or more. Early work on compound identification concentrated on carbon, oxygen, nitrogen, and sulfur species, but subsequent studies have also included halides, transition metals, and heavy metals. These capabilities in compound characterization make ESCA extremely powerful in environmental studies wherein oxidation state plays an important role in toxicity and environmental fate and transport.

ESCA is considered a surface technique because data are obtained only from the top 20 or so angstroms of the sample. Although the x-ray source penetrates much deeper into the sample, the excited electrons undergo many inelastic collisions which cause them to lose kinetic energy. Only electrons near and at the surface retain sufficient energy to escape the sample and enter the analyzer. The remainder are trapped within the sample or escape with reduced kinetic energy, producing the characteristic "tailing background" to the high binding energy (low kinetic energy) side of major photoelectron peaks (Figure 1). To examine the subsurface regions of a sample, a high energy argon ion beam may be used to etch away surface layers. By alternately etching and analyzing, a depth profile may be obtained to provide insight into particle formation mechanisms or surface enhancement of environmentally significant elements.

SCOPE OF WORK

The performance of this task required that appropriate samples be obtained for analysis in sufficient quantity to permit replication. These samples, consisting of fly ash, bottom ash, and spent bed materials, were subjected to ESCA analysis for elemental composition and limited oxidation state studies. Leachates were generated using the Level 1 aqueous procedure, and leachate solutions were screened for metals using ICP and for anions using ion chromatography. ESCA analyses of the leached solid samples were also performed.

The ESCA results were evaluated for reproducibility in replicate analyses. Measurements before and after leaching were used to evaluate the combined ESCA/leachate method for applicability to process stream wastes. In addition, elemental and anion analyses of the leachate solutions were used to corroborate the findings obtained by ESCA.

Acquisition of Samples

Samples used in this study were representative of potentially hazardous wastes from process streams and, for the most part, were available in sufficient quantity to permit replicate analyses. These samples consisted of fly ash and bottom ash from various combustion sources and several incinerator wastes. NBS SRM 1633a fly ash was used as a quality control sample.

Leachate Generation

Leachates were generated using the Level 1 aqueous leaching procedure in EPA-600/7-78-201 (October 1978).[3] This is the method specified for environmental assessment programs and consists of a 48-hour agitation extraction using deionized water at 20 ± 2°C without pH adjustment. The full procedure is presented in Section 5.

It was anticipated that, in addition to aqueous leachate generation, separate aliquots of some samples could be subjected to leaching with carbonic acid solution. The procedure is not currently a part of any formal environmental assessment scheme and was considered to be of secondary importance. Sample availability did not permit its being used in this study.

ESCA Analysis of Samples Before and After Leaching

Samples were analyzed using the ESCA-36 X-ray photoelectron spectrometer made by GCA/McPherson Instrument. For these analyses, the MgKα x-ray source with 1253.6 eV of energy was used as the excitation source. Capabilities of this technique have been described above. Complete analytical procedures are given in Section 5.

Waste samples were analyzed in their "as received" condition by mounting on sintered steel or sticky-tape substrates. Very small amounts of sample can easily achieve complete substrate coverage; however, blank substrates were analyzed to verify the absence of strong peaks in sample spectra which could be associated with the substrate material. After leaching, solid residues were similarly mounted on substrates for analysis or were analyzed, as captured, on the membrane filter. This choice depended on the amount of sample available and the particle size(s) and relied on the best judgment of the analytical team.

The ESCA analyses consisted of broadband scans of each sample to determine the surface elemental composition. Multiple scans were compiled, generally 3 to 10 in number, to provide increased sensitivity by increasing the signal-to-noise ratio. Short scans of selected elements were run to determine oxidation states of those elements. These included: carbon, oxygen, nitrogen, sulfur, lead, zinc, chromium, vanadium, and silicon.

Standards of the various oxidation states of these elements were analyzed to provide a comparative data base, and supplemental data were obtained from the literature.

Chemical Analysis of Leachates

Leachates from waste samples were analyzed for metals using inductively coupled argon plasma emission spectroscopy (ICP) and for anions by ion chromatography (IC). ICP was performed using the Jarrell-Ash Model 855, capable of measuring 27 elements simultaneously. These include Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sn, Sr, Ti, Tl, V, and Zn. IC was performed using the Dionex Model 14 with conductivity detection. It measures fluoride, chloride, sulfate, nitrate, bromide, phosphate, and other anions in one analysis run.

Data from chemical analysis of leachates was used to evaluate ESCA results from the solid wastes obtained before and after leaching. The species leached from the wastes were compared to changes observed in the sample surface using ESCA; agreement or disagreement was used to assess the utility of the ESCA/leachate technique for characterizing the leachability of process stream wastes.

Data Interpretation

For each sample analyzed, ESCA results were compared before and after leaching to determine changes in elemental and species composition which could be attributable to the leaching process. Significant increase or decrease in the relative concentration of individual elements was noted and, as possible, changes in oxidation state were evaluated. Results from chemical analyses of the leachates were compared to changes identified in the ESCA spectra for agreement or disagreement. The ability of ESCA to identify changes in sample composition caused by the leaching procedure (i.e., substantiated by IC and ICP) was evaluated in terms of accuracy and reproducibility.

SECTION 4

QUALITY ASSURANCE PROGRAM

All activities in this study were guided by a 14 point Quality Assurance Project Plan (QAPP) prepared according to the requirements set forth by the EPA.[4] The QAPP delineated procedures for chain-of-custody and analytical quality control including blanks, replicates and blind duplicates submitted with the samples under study. In addition, the QAPP presented the procedures and calculations to be used for each analysis performed and also described statistical evaluations to be made on the data. Because most of these procedures are standard requirements for work performed under EPA contracts, and because much of the information is included elsewhere in this report, these facets of the QAPP will not be repeated here. The audit report prepared by the Division QA Manager is included as Appendix A to this report.

INTERNAL QUALITY CONTROL CHECKS

Analytical internal QC activities and acceptance limits were summarized in Table 9-1 of the QA Project Plan. These are the standard procedures at GCA for the type of analytical methods used in this project. Acceptance limits are based on the capabilities of the technique and/or EPA QA requirements. The stated QC measures were followed and planned corrective actions were implemented as required.

PRECISION, ACCURACY AND COMPLETENESS

The results of replicate aliquots used to estimate precision are presented in Section 6 of this report; Table 1 lists the result table for each type of analytical procedure. The standard deviation of the mean of replicate analysis results is used to estimate precision; the result tables include this statistic.

Reference materials which were certified for surface composition were not available to check the accuracy of the ESCA work. However, two project samples were submitted as blind duplicates. Tables 26-28 in Section 6 compare analysis results on replicate aliquots of these samples. The chemical analysis of the leachates also provided corroborating data for the ESCA analyses. Literature values for differences in binding energy shifts for various lead compounds are compared with experimental lead speciation values in Table 32. Known QC samples with acceptance limits as stated in the QA Plan were run before each batch of project samples to ensure accuracy of the instrumentation.

TABLE 1. PRECISION DATA TABLES[a]

ESCA Analysis	
Before Leaching	
Triplicate aliquots of each sample	Tables 6-12, 18
Duplicate aliquots of each sample	Tables 13, 15-17
Blind duplicate samples	Tables 11, 12
After Leaching	
Duplicate aliquots of each sample	Tables 19, 21-24
ESCA Speciation	
Lead	
Triplicate aliquots of each sample	Table 31
Zinc	
Duplicate aliquots of each sample	Table 34
Ion Chromatography	
Leachates	
Triplicate aliquots of each sample	Tables 36-38
Blind duplicate samples	Tables 36, 38, 39, 40
Inductively Coupled Argon Plasma Spectrometry	
Leachates	
Triplicate aliquots of each sample	Tables 44-46
Blind duplicate samples	Tables 44, 46, 48, 49

[a] Tables are presented in Section 6 of this report.

Completeness is defined as the percentage of all measurements made which are judged to be valid. Of the 42 ESCA runs, 37 or 88 percent were judged valid. As noted in the Section 6 text, one run was judged nonrepresentative and two runs evidenced carbon contamination; two sample aliquots had low counts indicating loss in substrate handling. The ESCA speciation work also included one sample invalidated for low counts. Lead speciation achieved 92 percent completeness (12 of 13 samples valid) and the zinc speciation results were 88 percent complete (7 of 8 samples valid). The ion chromatography results were 100 percent complete but through a communication error, three sample aliquots planned for ICP analysis were not analyzed and one which was analyzed was thought to be an instrument check sample and was not reported. This resulted in a completeness of 71 percent (10 of 14 samples) but all reported ICP data was judged valid. Since the ICP work was not critical to the evaluation of the ESCA work, this was not deemed a serious quality problem.

PERFORMANCE AUDITS

Audit materials were not available for ESCA work and no EPA Performance Surveys presently deal with this technique. GCA routinely participates in the EPA Water Pollution (WP) and Water Supply (WS) Performance Evaluation Series which include all parameters analyzed by IC and ICP (except silicon) in this study. WP010 and WS011 samples were analyzed during this program.

SYSTEM AUDITS

GCA's QA Manager audited the project to check on the implementation of the QC measures outlined in the QA Project Plan. Her report is included in this report as Appendix A.

QUALITY PROBLEMS AND CORRECTIVE ACTIONS

Some anticipated types of quality problems associated with analytical instrumentation occurred and the planned corrective actions specified in the QA Plan were taken to resolve them. Following GCA's policy, these actions were documented in analysts' notebooks and were easily traceable in the audit of this project. No "long-term" corrective actions requiring initiation of a Corrective Action Request Form occurred.

SECTION 5

EXPERIMENTAL PROGRAM

An experimental program was conducted to evaluate an ESCA/leachate analytical scheme for assessing the leachability of waste materials from process streams. Of particular concern were fly ash and bottom ash from hazardous waste incineration. The original design of the experimental program was summarized in Section 3. Details of the program, as conducted, are given below.

ACQUISITION OF SAMPLES

Samples for this study were chosen to be representative of potentially hazardous wastes from process streams. Initially, reserve samples available from the GCA Sample Bank were checked for the availability of elemental, compound, and leachate data originally generated by other in-house projects. An additional sample was obtained from an industrial incinerator. Samples selected in this manner are listed in Table 2.

Data from experimentation with these first samples indicated that all were primarily aluminosilicate based and contained few elements of interest in terms of hazardous waste disposal. Species most often identified included hydrocarbon and carbonate (from limestone fluidized bed combustion), sulfate (combustion) and sulfide (from a sulfur recovery process waste). These species have previously been identified in combustion wastes and provided little insight into the capabilities of the ESCA technique. Additional samples were sought which might contain greater concentrations of trace metals.

In-house reserves of two samples from a syncrude-coke plant were known to contain fairly high concentrations of vanadium and nickel and had, in fact, shown substantial amounts of these metals leached by the EP toxicity method. This method utilizes an acetic acid buffer at pH 5 as the leaching solution and would be more rigorous than the aqueous leaching used in the Level 1 method. ESCA analysis of these two samples revealed vanadium above the detection limit but at insufficient concentrations to permit speciation. Nickel could not be detected in either sample. Therefore, additional samples were again sought, but this time from outside sources.

Notification had been received that Midwest Research Institute (MRI) was attempting to speciate chromium in waste feed and fly ash/bottom ash from a hazardous waste incinerator. ESCA was being considered as a possible means for distinguishing Cr(III) from Cr(VI) and samples could be provided to us to attempt this speciation. The samples listed in Table 2 include waste feed and

TABLE 2. SUMMARY OF SAMPLES OBTAINED AND NUMBER OF ALIQUOTS LEACHED AND ANALYZED BY ESCA

GCA No.	Description	ESCA Before Leaching[a]	Leachate Generation	ESCA After Leaching[b]	Remarks
Inhouse Samples					
3610	FBC (Coal) Cyclone Ash	3	3	2	Uninteresting sample composition
9949	CAFB (Oil) RESOX Ash	3	3	2	Uninteresting sample composition
24616	Incinerator Baghouse Ash	3	3	2	Uninteresting sample composition
21369	Syncrude-Coke Bed Ash	1	None	--	Insufficient trace metal content for speciation
21370	Syncrude-Coke Fly Ash	1	None	--	Insufficient trace metal content for speciation
MRI Phase I (Rec'd 11/82)					
27745	Incinerator Particulate Filter	3[b]	1	2	Sample limited
27746	Incinerator Particulate Filter	2[b]	1	2	Sample limited
27747	Waste Feed	2	None	--	Composition not suitable for leaching
27748	Waste Feed	2	None	--	Composition not suitable for leaching
MRI Phase II (Rec'd 1/83)					
29173	Kiln (Bottom) Ash	3	None	--	Uninteresting sample composition
29174	Filter Particulate (Kiln Fly Ash)	3	1	2	Sample limited
QC Samples					
1633a	NBS SRM Coal Fly Ash	3	1	NA[c]	Leachate for IC/ICP internal QC
029-QC-1	Blind Duplicate	3	1	NA	Internal QC of ESCA
029-QC-2	Blind Duplicate	3	1	NA	Internal QC of ESCA

[a] Analyses performed on separate aliquots unless otherwise noted.

[b] Analyses performed on replicates from same aliquot.

[c] Not analyzed.

ash samples submitted by MRI as part of the chromium speciation study. In addition to chromium, the filter particulate samples contained significant amounts of lead and zinc which were also subjected to oxidation state analysis. These samples were considered to be the most suitable for determining the capabilities of ESCA.

LEACHATE GENERATION

Samples subjected to triplicate leachate generation were the bulk solids and QC samples obtained in the initial search for samples. These were GCA Nos. 3610, 9949, and 24616. Procedures were as described herein.

The aqueous leaching procedure specified by the Level 1 Manual[3] is based on the Proposed Method for Leaching of Waste Materials, ASTM, 1916 Race Street, Philadelphia, PA 19103. It consists of agitating a known amount of solid sample with deionized, distilled water (DDW) and filtering the extract prior to analysis. Apparatus and reagents required to accomplish the Level 1 leaching of bulk solids are as follows:

- Agitation equipment--Agitation equipment to produce constant movement of the aqueous phase equivalent to that of a reciprocating platform shaker operated at 60 to 70 one-inch (25 mm) strokes per minute without incorporation of air is suitable. Equipment used must provide continuous operation without heating the sample being agitated.

- Membrane filter assembly--A borosilicate glass or stainless steel funnel with a flat, fluted base of the same material, and membrane filters are required.

- Containers--Round, wide-mouth bottles of linear polyethylene (LPE) are suitable for most bulk solids samples and are compatible with the anion and metals analyses. Usually one or two liter bottles are used with approximately 175-g or 350-g samples to provide ample solution for the analyses planned. The combined solid sample and leaching solution should occupy 80 to 90 percent of the bottle volume. The closure must be water tight, and if gases are released from the sample, provision must be made for their venting from the bottle. Cleaning of the bottles must not introduce anions expected to be measured by IC. (Because sample quantities were limited, aliquots for this study consisted of 45 grams of sample plus 180 ml DDW in 250 ml bottles.)

- Test water--Reagent grade, deionized and distilled.

The leachate generation procedure consists of the following steps:

- Grind the material, if necessary, to pass through a 9.5 mm (3/8-in.) standard sieve. (Grinding was not performed in this study because the waste is not ground before disposal and grinding would change the surface exposed for ESCA analysis.)

- Dry the sample 18 ± 2 hr at 104 ± 2°C. Cool to room temperature in a dessicator.
- Weigh a representative portion of the material to be tested. Record the value to ± 1g.
- Place the weighed portion of sample into the container to be used in the shake test.
- Add to the container a volume of test water equal in milliliters to four times the weight in grams of the aliquot to be leached.
- Close the container and place it on the agitation equipment.
- Agitate continuously for 48 ± 0.5 hr at 20 ± 2°C.
- Open the containers. Observe and record any changes in the sample and leaching solution.
- Separate the bulk of the aqueous phase from any solid or nonaqueous phases by decantation, centrifugation, or filtration through filter paper, as appropriate. Vacuum filter the aqueous phase through a 0.45 μm membrane filter, if necessary.
- Transfer the filtrate to sample bottles of a size such that the entire bottle is filled. Close and label. Preserve the filtrate in a manner consistent with the chemical analyses to be performed; in this case, acid preservation is not recommended for the total leachate because of introduction of anions to the sample. (One aliquot was refrigerated for IC analyses and a separate portion was acidified for ICP analysis.)
- Place the leached solid and membrane filter in appropriate containers and dry at 104 ± 2°C for 18 hours. Cool in a desiccator and store in a tightly capped container until analysis. Repeat drying for 1 hour and desiccation, if necessary, before analyzing.

Filter particulate samples obtained from MRI required a modification to the above procedure. Insufficient sample was available to remove particulate from the filter for leachate generation and then be able to recover enough for ESCA analysis. Therefore, an aliquot of each filter was placed in a petri-dish with 25 ml of DDW and gently agitated by hand several times over the next 48 hours. As much as possible, the particulate was kept on the sample filter to facilitate ESCA analysis. The leachate was filtered into 25 ml volumetric flasks and made to volume for IC and ICP analysis. This filter was also retained for ESCA analysis. After IC analyses were conducted, the aliquots were acidified to preserve them for metals analysis. Samples subjected to this modified leaching procedure were GCA Nos. 27745, 27746, and 29174.

ESCA ANALYSIS OF SOLID SAMPLES

Insofar as possible, samples were analyzed in triplicate by ESCA. These data were used to determine precision achievable by the ESCA technique. Several of the samples were not available in sufficient quantity to permit triplicate analysis and only duplicate measurements could be made. Table 2 summarizes ESCA analyses and leachate generations conducted on the samples used in this study. Comments are made regarding why fewer then three aliquots were analyzed. Procedures followed for ESCA analyses are delineated below.

ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

- Fine particulate and waste samples were pressed on to sintered steel substrates and coarser particulate matter was placed onto sticky tape in copper window sample holders. A blank was prepared for each type of substrate used. Samples and standards were treated identically. Substrates were covered completely by sample material.
- Up to eight samples were placed in the sample wheel, and the wheel was placed in the source chamber. The source was evacuated to 10^{-6} torr and the cryopump was activated.
- Spectral parameters were defined and entered into the pdp8e computer for execution. These parameters include the binding energy range, the duration of counting at each data point and the number of scans to be compiled for that range and that sample. Spectra used in this study are defined in Table 3. Except for all Au4f and Ag3d, spectra were generally accumulated for 10 or 20 scans.

TABLE 3. SELECTED SCAN PARAMETERS FOR ESCA ANALYSIS

Spectrum	Binding energy range (eV)	Number of data points	Energy step size (eV)	Length of scan (eV)
Broadband	1000-0	1003	1.0	1000
Carbon 1s	295-275	126	0.16	20
Oxygen 1s	540-520	126	0.16	20
Sulfur 2p	175-155	126	0.16	20
Chromium 2p	590-570	126	0.16	20
Vanadium 2p	540-500	251	0.16	40
Lead 4f	150-130	126	0.16	20
Zinc 3p	95-75	126	0.16	20
Silver 3d	380-360	126	0.16	20
Gold 4f	90-80	126	0.08	10

- Spectra were retrieved by plotting on the X-Y recorder (Figure 2) and electron counts were recorded for high and low energy endpoints of the scan and for maximum peak height in the energy range scanned. Binding energy was used to identify the elements present, and relative abundance of the elements was calculated by dividing peak height by photoelectron sensitivity and normalizing over total response. The formula for this calculation is provided elsewhere in Section 5. Results were reported as percent atomic and could also be calculated as percent by weight.

- Speciation required that short scans of the elements of interest and the carbon 1s photoelectron be taken. Precise binding energy was determined from spectral plots, and ΔE from carbon 1s to the element of interest was calculated. The ΔE for the sample was then compared to standards for identification of the species or oxidation state present.

CHEMICAL ANALYSIS OF LEACHATES

Trace metals in sample leachates were analyzed by inductively coupled plasma emission spectrometry using EPA Method 200.7[5] for water and wastes, as follows:

- The instrument was set up as specified in the Jarrell-Ash manual[6] and allowed to warm up for 30 minutes prior to calibration.

- The sample matrix was programmed into the computer.

- The instrument was profiled and calibrated using mixed calibration standards and the system flushed with the calibration blank between each standard.

- An EPA trace metals concentrate was analyzed and the resulting values entered on the appropriate control chart. The values obtained must be within the established control limits or the instrument must be recalibrated.

- The samples were analyzed and the system was flushed with the calibration blank between each sample.

- If the method of standard addition was required, procedures specified in the GCA Analytical Procedures Manual, Volume 1,[7] were followed.

Leachates were analyzed for anions using ion chromatography (IC). Samples and standards were treated identically during analysis. The following procedures were used:

- A syringe filtering system was attached to the outlet of the syringe and three or more milliliters of solution were placed in the syringe barrel. Air was expelled from the syringe and filter unit and the system was then attached to the ion chromatograph's injection valve. Although the injection loop is only 100 μl in volume, it is common

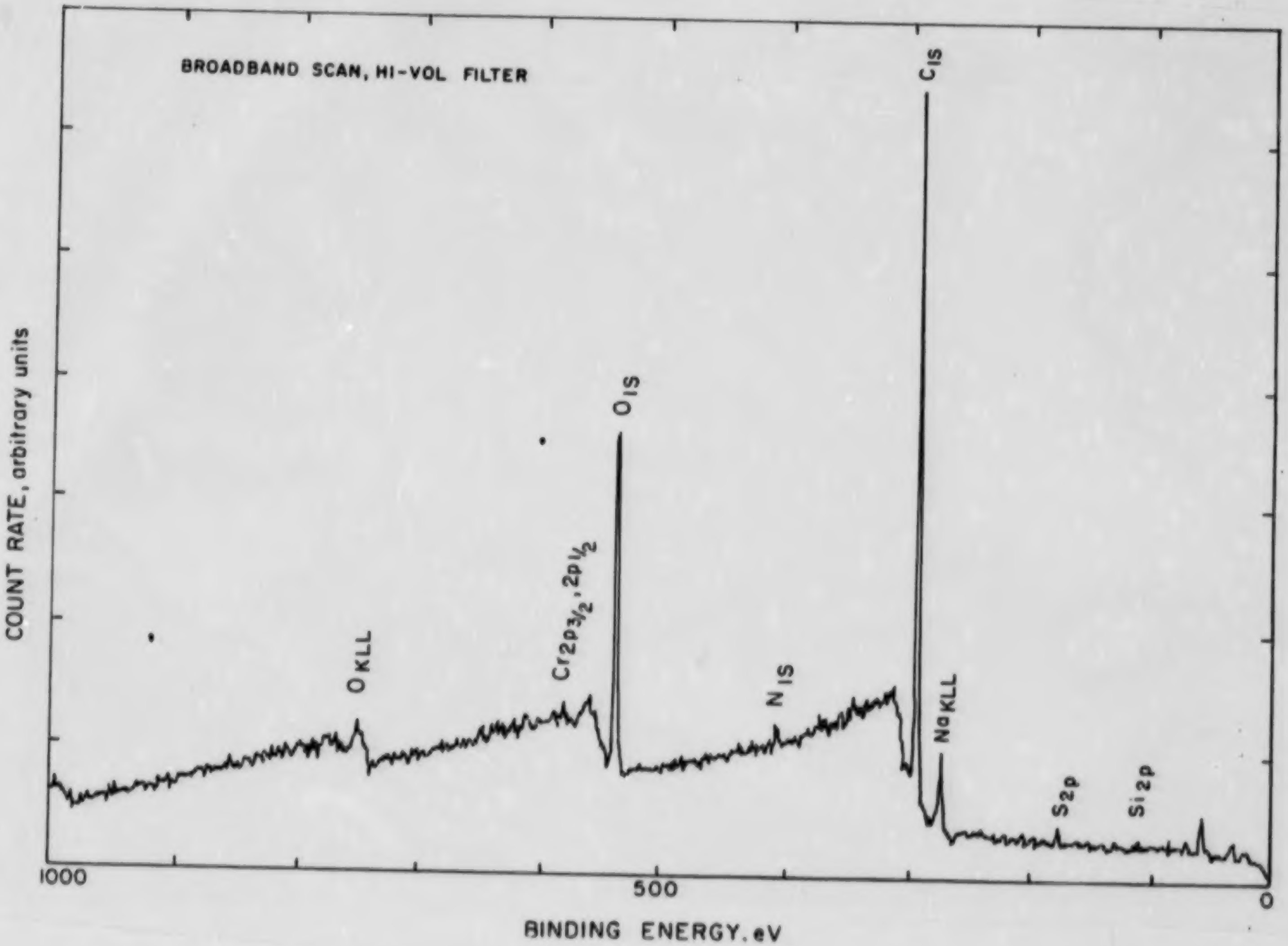


Figure 2. Broadband ESCA spectrum of a hi vol filter.

practice to flush 1 to 2 ml into and through the loop prior to injection. This is to ensure that no sample from the previous injection remains in the loop.

- Instrument conditions for standard anion analyses and conductivity detection are given in Table 4. The procedures required no modification for the analyses conducted in this project.

TABLE 4. OPERATING PARAMETERS FOR IC

Separator column	4 x 250 mm
Suppressor column	9 x 100 mm
Precolumn	4 x 50 mm
Injection loop	100 µl
Eluent	0.003 M $NaHCO_3$/0.0024 M Na_2CO_3
Flow rate	30 percent
Regenerant	1 N H_2SO_4
Analysis time	20 minutes
Maximum back-pressure	600 psi

- The elution of the ions was recorded on a strip chart in which the elution time (from time of injection) is used to identify each of the ions present. The peak height was used to calculate the concentration of each run. Standard curves plotting peak height against concentration (µg/ml) were made for each of the ions to be quantified. If the sample concentration were above the standards plotted on the day of analysis, an aliquot of the sample was diluted and analyzed.

DATA REDUCTION

Data from elemental analyses by ESCA is reported as percent atomic and, for some samples, percent by weight of the surface. Quantification in percent atomic is accomplished by measuring the peak height of the most intense line of each element, dividing the intensity for each line by its sensitivity factor (Table 5) and normalizing each value to the total surface intensity. The resulting data indicate the percentage of total "surface" atoms attributable to each element. The calculation can be summarized as follows:

$$A_i = \frac{\frac{h_i}{F_i}}{\sum_{i=1}^{n} \frac{h_i}{F_i}} \times 100$$

TABLE 5. SELECTED ELEMENTAL SENSITIVITY FACTORS (F) FOR THE ESCA-36[a]

Element	Electron	Sensitivity Factor
Carbon	1s	241
Oxygen	1s	431
Calcium	2p 3/2	1215
Sodium	KLL	1381
Sulfur	2p	497
Silicon	2p	596
Aluminum	2s	226
Chlorine	2p	567
Phosphorus	2p	480
Fluorine	1s	562
Lead	4f 7/2	4317 (±20%)
Zinc	3p	662 (±40%)
Tin	3d 5/2	2990 (±25%)
Titanium	2p	953
Chromium	2p	744
Iron	2p 3/2	619
Copper	3p	823
Potassium	2p 3/2	956
Vanadium	2p 3/2	1026

[a] These sensitivity factors are based on data published in Reference 2.

where A_i = % atomic of element i

h_i = peak height of most intense electron of element i

F_i = sensitivity factor for that photoelectron

n = total number of elements detected in the sample

100 = conversion to percent

To calculate as percent by weight, the following formula is used:

$$W_i = \frac{\frac{h_i}{F_i} \times EW_i}{\sum_{i=1}^{n} \left(\frac{h_i}{F_i} \times EW_i \right)} \times 100$$

where W_i = percent by weight of element i

EW_i = equivalent weight of element i

All data from ICP and IC analyses of the leachates are reported in units of µg/ml. All data may be converted to µg/g using the following equation.

$$X_w = [X_v \times V \times d.f.] \quad W$$

where X_w = reported value, µg/g

X_v = reported value, µg/ml

V = leachate volume, milliliters

d.f. = dilution factor

W = sample weight leached, grams

Appropriate blank corrections have been applied in all cases.

SECTION 6

RESULTS AND DISCUSSION

Samples were subjected to elemental analyses and speciation of selected elements of environmental significance before and after aqueous leaching. Samples analyzed in triplicate (using separate aliquots) were used to determine the precision of the ESCA analytical technique. No standard materials are available with which to evaluate its accuracy.

Leachates generated in triplicate by the Level 1 aqueous extraction method were analyzed by ion chromatograhy (IC) and inductively coupled plasma (ICP) spectrometry to evaluate the precision of the leaching procedure. These data were compared to changes in the ESCA results of measurements taken before and after the leaching to corroborate those findings. Insofar as was possible, ESCA speciation was correlated to changes in samples attributable to leaching.

ELEMENTAL ANALYSES BY ESCA

ESCA data for samples before leaching are presented in Tables 6 through 18. Data after leaching are given in Tables 19 through 24. Included are calculations of mean ($\overline{X}$), standard deviation (S) and percent relative standard deviation (RSD) for each set of triplicate data. Average concentrations are calculated for samples analyzed in duplicate. For samples also submitted as blind QC samples for ESCA, control limits defined as $\overline{X} \pm 2S$ are presented so that the quality of the precision data can be evaluated. No elemental analysis data were calculated for GCA 21369, 21370 or 29173. These samples were screened for trace metal content and were found to contain insufficient concentration and/or variety to warrant their being used further in this study. Spectra were printed and have been retained in the project file and are included in Appendix B.

Sample Substrate

Two types of substrates were used for mounting free particulate samples, that is, particulate not captured on filters. These substrates were sintered stainless steel (SS) pads 1 cm x 2 cm in size or sticky tape (ST) attached to the underside of a copper-window type sample holder. The Cu-window holder forms a rigid frame to facilitate handling of the samples pressed onto the tape. It is particularly useful for large size particles that cannot be accomodated by SS substrates. The Cu-windows without tape are used to hold filter samples onto the spring-loaded pads on the eight-position sample wheel. The window is sufficiently large enough to prevent the holder from falling within the analytical field of the ESCA.

TABLE 6. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 3610, BEFORE LEACHING

Element	Run 1	Run 2	Run 3	$\bar{X}$	S	RSD (%)	Control Limits
Carbon	45	49	48	47	2.1	4.5	43 - 51
Oxygen	38.2	32.6	33.4	34.7	3.0	8.6	28.7 - 40.7
Calcium	3.4	2.5	2.9	2.9	0.45	15.5	2.0 - 3.8
Sodium	0.5	0.4	0.4	0.4	0.06	15	0.3 - 0.5
Sulfur	3	3.7	3.9	3.5	0.47	13	2.6 - 4.4
Silicon	4.7	5.2	5.5	5.1	0.40	7.8	4.3 - 5.9
Aluminum	6.2	6	6.1	6.1	0.1	1.6	6.0 - 6.2

TABLE 7. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 9949, BEFORE LEACHING

Element	Run 1	Run 2	Run 3	$\bar{X}$	S	RSD (%)
Carbon	62.3	86.5	90.6	79.8	15.3	19
Oxygen	27	7.5	5.8	13	12	92
Sodium	ND	0.4	ND	-	-	-
Sulfur	2	3.1	3	2.7	0.6	22
Silicon	2.8	0.8	0.6	1.4	1.2	86
Aluminum	6	2	ND	4[a]	-	-

[a] Average of n=2 measurements.

TABLE 8. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 24616, BEFORE LEACHING

Element	Run 1	Run 2	Run 3	$\overline{X}$	S	RSD (%)	Control Limits
Carbon	44	37	35	39	4.7	12	30 - 48
Oxygen	37.6	41.6	38.2	39.2	2.2	5.6	34.8 - 43.6
Calcium	8.3	9.0	9.0	8.8	0.40	4.5	8.0 - 9.6
Sodium	0.8	0.7	0.7	0.7	0.06	9	0.6 - 0.8
Sulfur	4.4	5.3	6.1	5.3	0.85	16	3.6 - 7.0
Silicon	1	2	2	2	0.6	30	0.8 - 3
Aluminum	2.3	2.7	3.2	2.7	0.45	17	1.8 - 3.6
Phosphorus	2	2	3	2	0.6	30	0.8 - 3

TABLE 9. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 24616, BEFORE LEACHING[a]

Element	Run 1	Run 2	Run 3	$\overline{X}$	S	RSD (%)	Control Limits
Carbon	43.7	36.7	34.8	38.4	4.7	12.2	29 - 48
Oxygen	37.6	41.4	37.9	39.0	2.1	5.4	34.8 - 43.2
Calcium	8.4	9.0	9.0	8.8	0.3	3.4	8.2 - 9.4
Sodium	0.8	1.0	0.7	0.8	0.2	25	0.4 - 1
Sulfur	4.4	5.2	6.1	5.2	0.9	17	3.4 - 7.0
Silicon	1	2	2	2	0.6	30	1 - 3
Aluminum	ND	ND	3.4	-	-	-	-
Chlorine	2.3	2.7	3.2	2.7	0.45	17	1.8 - 3.6
Phosphorus	2	2	3	2	0.6	30	1 - 3

[a] Second quantification performed on same spectra used to generate data in Table 8; used to verify reproducibility of the calculation.

TABLE 10. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 1633a, BEFORE LEACHING

Element	Run 1	Run 2	Run 3	$\overline{X}$	S	RSD (%)	Control Limits
Carbon	40	45	41	42	2.6	6.2	37 - 47
Oxygen	44.3	40.1	42.6	42.3	2.11	5.0	38.1 - 46.5
Sodium	ND	0.4	0.2	0.3 (n=2)	-	-	-
Sulfur	3	2.8	3	3	0.1	3	2.8 - 3.2
Silicon	6.3	6.1	6.8	6.4	0.4	6.3	5.6 - 7.2
Aluminum	6.9	5.5	6.4	6.3	0.7	11	4.9 - 7.7

TABLE 11. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 029-QC-1, BEFORE LEACHING

Element	Run 1	Run 2	Run 3	$\overline{X}$	S	RSD (%)	Control Limits
Carbon	45	45	38	43	4.0	9.2	35 - 51
Oxygen	36.2	36.2	42.2	38.2	3.5	9.2	31.2 - 45.2
Calcium	3.3	3.0	3.4	3.2	0.2	6.3	2.8 - 3.6
Sodium	ND	0.6	ND	-	-	-	-
Sulfur	3.6	3.5	3	3.4	0.3	8.8	2.8 - 4.0
Silicon	5.0	5.0	5.5	5.2	0.3	5.8	4.6 - 5.8
Aluminum	6	6.6	6	6	0.3	5	5 - 7
Titanium[a]	0.9	ND	ND	-	-	-	-
Iron[a]	ND	ND	1	-	-	-	-

[a] Identification unconfirmed.

TABLE 12. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 029-QC-2, BEFORE LEACHING

Element	Run 1	Run 2	Run 3	$\overline{X}$	S	RSD (%)	Control Limits
Carbon	37	56.5	39	44	11	25	22 - 66
Oxygen	38.6	29.1	41.2	36.3	6.4	18	23.5 - 49.1
Calcium	9.2	5.5	9.7	8.1	2.3	28	3.5 - 12.7
Sodium	0.6	0.5	0.8	0.6	0.2	33	0.2 - 1.0
Sulfur	3.9	2	3.3	3	1	33	1 - 5
Silicon	2.6	1	1	2	0.9	45	0.2 - 4
Aluminum	4	3	2	3	1	33	1 - 5
Chlorine	1	1	2	1	0.6	60	0 - 2
Phosphorus	3	1	ND	2[a]	-	-	-

[a] Average of n = 2 measurements.

TABLE 13. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 27745, BEFORE LEACHING

Element	Run 1	Run 2	Run 3[a]	$\overline{X}$[b]
Carbon	25	25	55	25
Oxygen	41	39.7	25	40
Calcium	6.3	6.3	3.4	6.3
Sulfur	2	3	1	3
Silicon	3	2.6	2	3
Chlorine	9.4	9.3	5.7	9.4
Phosphorus	5.8	5.8	4.1	5.8
Fluorine	2	2	ND	2
Lead	1.4	1.4	0.8	1.4
Zinc	4.2	4.0	2.7	4.1
Tin[c]	ND	0.3	0.3	-
Vanadium[c]	ND	0.9	ND	-

[a] Run 3 believed to show carbon contamination from source chamber; data considered invalid.

[b] Average of Run 1 and Run 2 only.

[c] Identification unconfirmed.

TABLE 14. ESCA RESULTS (PERCENT ATOMIC):
SAMPLE 27746, BEFORE LEACHING

Element	Run 1	Run 2[a]
Carbon	29	52
Oxygen	41.6	28
Calcium	4.1	2.3
Sulfur	3.8	3
Silicon	3.5	3.1
Chlorine	9.1	5.9
Phosphorus	4.7	3.2
Fluorine	1	0.8
Lead	0.2	0.2
Zinc	2	1
Tin	0.3	ND
Titanium	0.9	ND
Iron	ND	0.7

[a] Run 2 believed to show carbon contamination from source chamber; data considered invalid.

TABLE 15. ESCA RESULTS (PERCENT ATOMIC):
SAMPLE 27747, BEFORE LEACHING

Element	Run 1[a]	Run 2[b]	$\bar{X}$[c]
Carbon	85.1	85.9	85.5
Oxygen	8.8	11	9.9
Sulfur	1	ND	-
Chlorine	1	1	1
Lead	1.4	1.2	1.3
Zinc	ND	0.5	-
Titanium	0.8	ND	-
Chromium	1	0.4	0.7

[a] Run 1 accumulated NS=5 passes.

[b] Run 2 accumulated NS=10 passes.

[c] Average of n=2 measurements.

TABLE 16. ESCA RESULTS (PERCENT BY WEIGHT: SAMPLE 27747, BEFORE LEACHING

Element	Run 1[a]	Run 2[b]	$\overline{X}$[c]
Carbon	62.3	66.6	64.5
Oxygen	8.6	11	9.8
Sulfur	3	ND	-
Chlorine	3	3	3
Lead	18	16	17
Zinc	ND	2	-
Titanium	2	ND	-
Chromium	3	2[d]	3

[a] Run 1 accumulated NS=5 passes.

[b] Run 2 accumulated NS=10 passes.

[c] Average of n=2 measurements.

[d] Values calculated as 1.5 but significant figures require that it be reported as 2.

TABLE 17. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 27748, BEFORE LEACHING

Element	Run 1[a]	Run 2[b]	$\overline{X}$[c]
Carbon	87.2	90.9	89.1
Oxygen	11	7.8	9.4
Silicon	2	1	2

[a] Run 1 accumulated NS=5 scans.

[b] Run 2 accumulated NS=10 scans.

[c] Average of n=2 measurements.

TABLE 18. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 29174, BEFORE LEACHING

Element	Run 1	Run 2	Run 3	$\overline{X}$	S	RSD (%)
Carbon						
hydrocarbon	17.2	13.8	16.4	15.8	1.8	11
other	ND	ND	13.5	–	–	–
Oxygen	52.2	51.6	40.5	48.1	6.6	14
Sodium	1.8	1.7	1.2	1.6	0.3	19
Silicon	9.4	9.4	7.4	8.7	1.2	14
Chlorine	1.7	2.7	2.9	2.4	0.6	25
Phosphorus	3.1	3.7	1.9	2.9	0.9	32
Lead	2.2	2.2	1.8	2.1	0.2	10
Tin	4.1	4.7	3.7	4.2	0.5	12
Iron	2.8	ND	ND	–	–	–
Chromium	1.4	1.5	1.3	1.4	0.1	7
Copper	ND	3.0	5.1	4.1[a]	–	–
Potassium	4.1	5.6	4.7	4.6	0.87	18

[a] Average of n=2 measurements.

TABLE 19. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 3610, AFTER LEACHING

Element	Run 1	Run 2	$\overline{X}_{n=2}$
Carbon	42	42	42
Oxygen	41.9	42.9	42.4
Calcium	4.2	3.7	4.0
Sulfur	0.9	0.9	0.9
Silicon	5.5	6.2	5.9
Aluminum	5	4	5

TABLE 20. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 9949, AFTER LEACHING

Element	Run 1[a]
Carbon	44
Oxygen	42
Sulfur	3
Silicon	ND
Aluminum	5
Iron	6.0

[a] Second aliquot lost from substrate; analysis not performed.

TABLE 21. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 24616, AFTER LEACHING

Element	Run 1[a]	Run 2[b]	$\bar{X}_{n=2}$
Carbon	27	27	27
Oxygen	52.9	51.1	52.0
Calcium	4.4	4.0	4.2
Sodium	0.6	0.8	0.7
Silicon	4.1	4.4	4.3
Aluminum	9	9.8	10
Chlorine	0.8	1	0.9
Phosphorus[a]	2	2	2

[a] Identification unconfirmed (trace).

TABLE 22. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 27745, AFTER LEACHING

Element	Run 1	Run 2	$\bar{X}_{n=2}$
Carbon	27	22	25
Oxygen	52	54	54
Silicon	5	5.3	5
Chlorine	3	2	3
Phosphorus	6	7.9	7
Lead	4.5	4.4	4.5
Zinc	4.2	4.1	4.2
Tin	ND	0.7	-

TABLE 23. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 27746, AFTER LEACHING

Element	Run 1	Run 2[a]
Carbon	18	72
Oxygen	59.6	23
Silicon	7.5	2
Chlorine	2	ND
Phosphorus	7.1	2
Lead	1.2	0.3
Zinc	2.6	0.8
Iron	1	ND
Potassium	1	ND

[a] Run 2 was mounted on sticky tape substrate and gave low overall electron counts; suspect that sample flaked off of substrate and that high carbon is actually signal from the adhesive; data rejected.

TABLE 24. ESCA RESULTS (PERCENT ATOMIC): SAMPLE 29174, AFTER LEACHING

Element	Run 1	Run 2	$\bar{X}_{n=2}$
Carbon	21	19	20
Oxygen	51	55	53
Calcium[a]	1	ND	–
Sodium	0.6	0.8	0.7
Silicon	8.5	9.0	8.8
Chlorine	2	ND	2
Phosphorus	4	4	4
Lead	4.4	4.5	4.5
Tin	4.0	4.0	4.0
Iron	2	2	2
Chromium	1	2	2

[a] Identification unconfirmed.

Mounting particulate samples on SS and/or ST substrates holds the hazard that incomplete coverage of the substrate may occur during preparation or as a result of handling. Therefore, substrate blanks were analyzed in triplicate, so that typical ESCA spectra would be available to compare with the results of sample analysis. Representative spectra of the substrate blanks are shown in Figure 3 (SS Blank) and Figure 4 (ST Blank). The SS blank contains carbon, oxygen, iron and chromium as major components and has a characteristic "hump" in the 900-650 ev range. The ST blank contains carbon (two species) and oxygen, and aliquots occasionally show contamination of silicon and aluminum from ambient air particulates. Its most characteristic feature is that carbon is present at about 90 percent atomic. ST substrate breakthrough is more difficult to detect than that from SS substrate. (Low electron counts can be another indicator of poor substrate coverage.)

If substrate breakthrough were suspected from looking at the spectra obtained, the aliquot in question would be carefully scrutinized upon removal from the instrument to determine whether substrate had been exposed during analysis. If such a problem occurred, the data for the suspect aliquot were rejected and excluded from data interpretation. As time permitted, replacement aliquots were prepared and analyzed.

In addition to the analysis of substrate blanks, samples were subjected to a substrate effects test in which separate aliquots of the same sample were mounted on the two different substrates. Elemental composition data were then evaluated for significant differences in qualitative and quantitative results. Table 25 compares results for sample 3610 on each substrate. Qualitatively, the results are excellent, even to the detection of two species of carbon in the sample. Quantitatively, the results for major components are excellent; however, minor components (<10 percent atomic) show greater scatter, up to 30 percent relative difference. Because no consistent bias was observed for one or the other of the substrates, it was determined that these differences could, in part, be attributable to sample inhomogeneity. Therefore, either substrate was considered to be acceptable for the analyses planned for this study. Except for filter particulate samples which used Cu-windows to assist mounting and waste samples (27747 and 27748) which were only amenable to mounting on SS substrates, all samples were mounted on ST substrates for the ease and economy of their use. Occasional substrate break-through was found with ST substrates and is noted in the data tables where appropriate.

ESCA Precision

ESCA analyses of particulate samples do not meet the estimates of ± 5 percent RSD stated by Hercules, etal,[8] primarily because the samples used in this investigation are known to be inhomogenous. For fine particulate such as 3610, 24616, and the filter capture, this inhomogeneity is less significant than for the pebble-sized 9949. Fine particulate samples are spread onto a sticky tape or sintered steel substrate forming an aliquot comprised of thousands of individual particles from the sample. The ESCA signal produced by these samples is an average of many individual particles and tends to reduce the apparent inhomogeneity of the sample. Sample 9949 with its particle size on the order of 1 cm x 1 cm required that only one

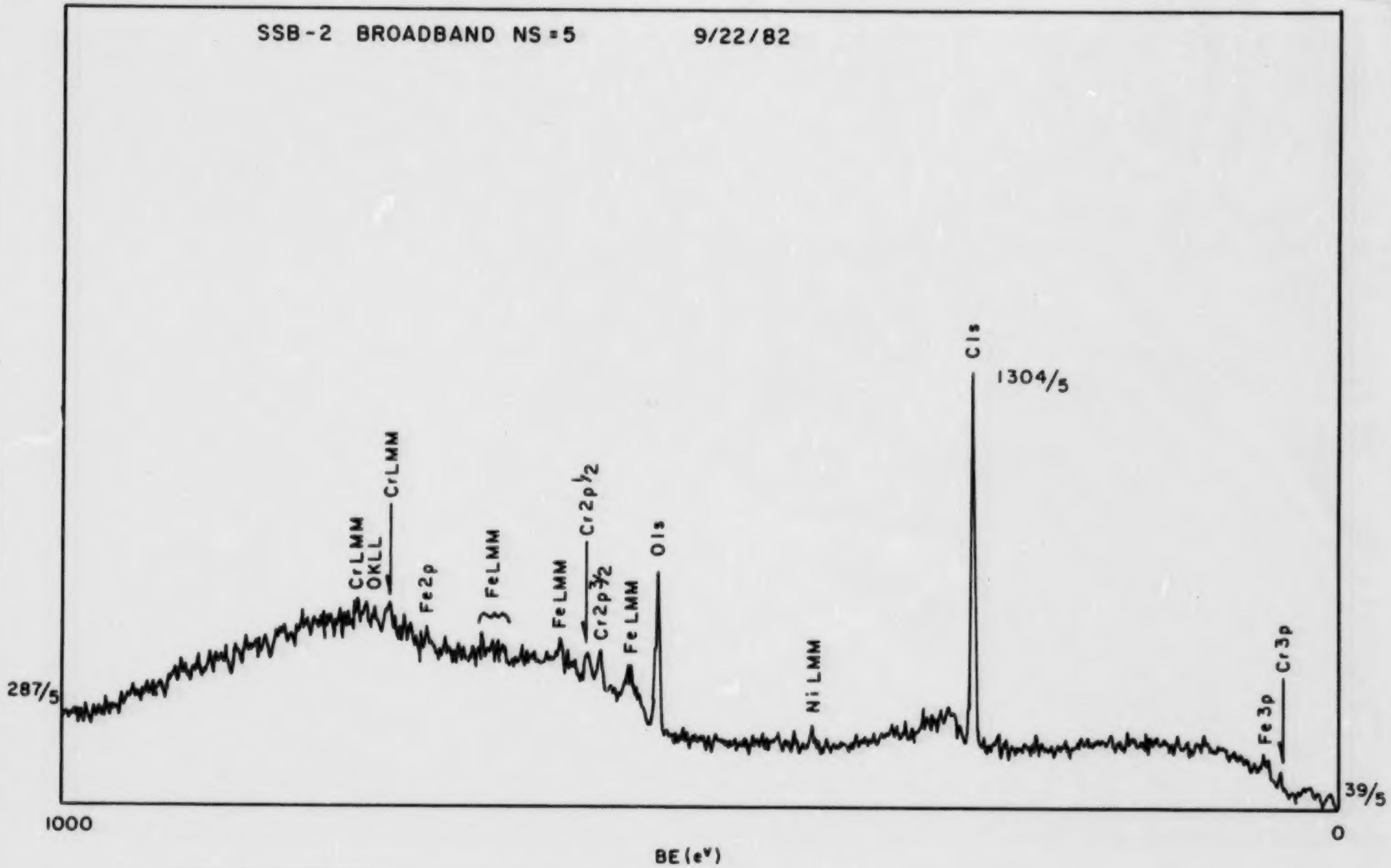


Figure 3. Stainless steel substrate blank.

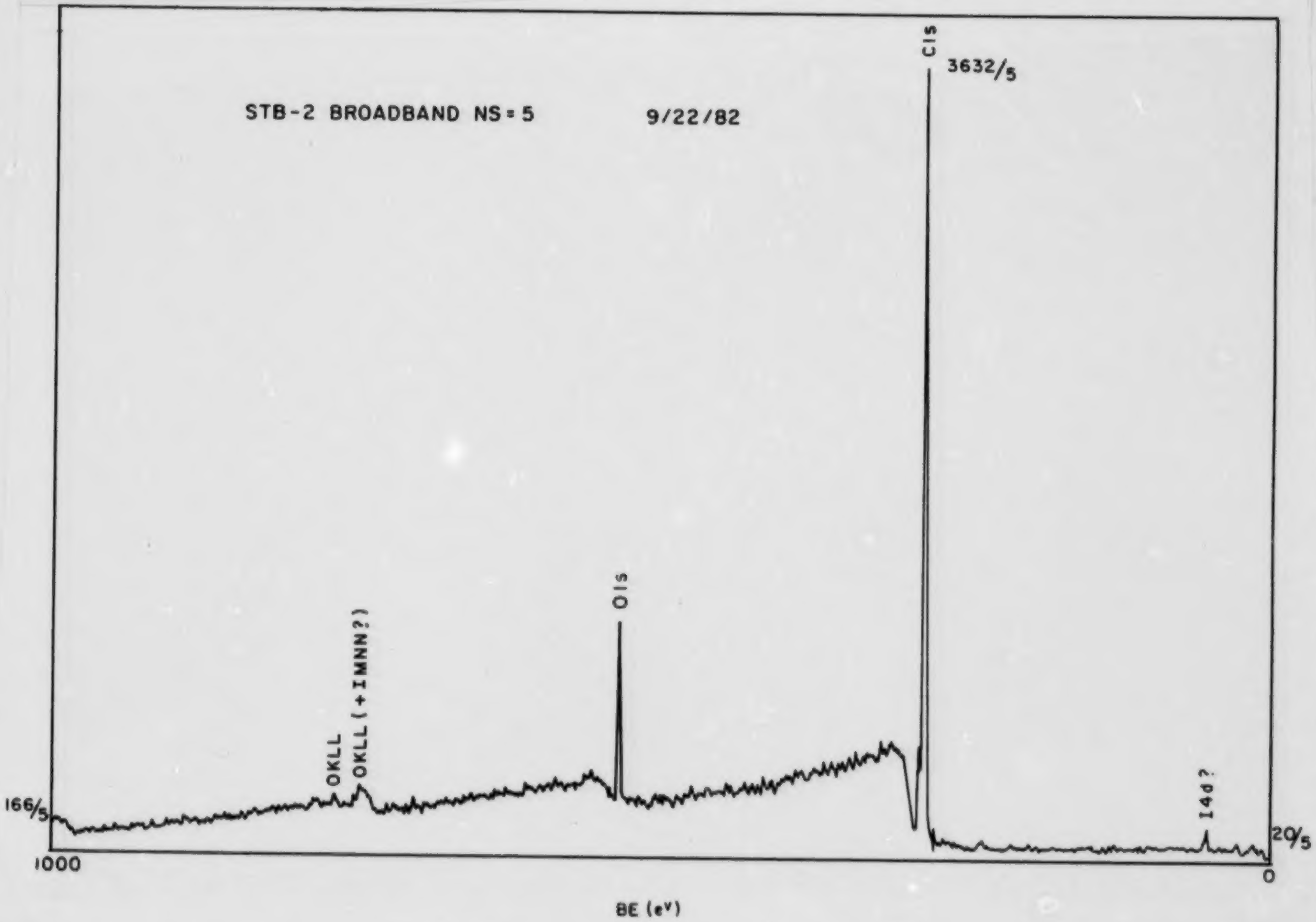


Figure 4. Sticky tape substrate blank.

TABLE 25. EFFECT OF SUBSTRATE ON CONCENTRATIONS RESULTS BY ESCA[a]

Element	Percent atomic		Percent difference
	SS[b]	ST[c]	
Carbon			
hydrocarbon	29	29	0
other	17	17	0
Oxygen	35.6	35.5	0.3
Calcium	3.1	3.5	12
Sulfur	2.8	3.7	28
Silicon	4.9	5.7	15
Aluminum	7.5	6	22

[a] Sample 3610 used for this test.

[b] SS = stainless steel (sintered) substrate.

[c] ST = sticky tape substrate mounted in Cu-window type sample holder.

particle be mounted on sticky tape per aliquot. Therefore, differences in the individual particles and the irregular particle surface produced more scattered ESCA results. This is reflected in the data.

Note that for 9949 before leaching the percent RSD ranges from 19-92 percent, but for most of the other samples, values greater than 15-20 percent RSD are uncommon and are usually limited to elements present at low concentrations where minor changes in peak height can result in large differences in final concentration.

One exception to this is 029-QC-2 for which percent RSD ranges from 18 to 60. A closer examination of the data from individual aliquots indicates that Run 2 may not be representative of the major portion of the material. Sample 029-QC-2 was inserted as a blind duplicate of 24616. A study of the individual aliquot results reveals that Run 1 and Run 3 have one and three values, respectively, that fall outside the control limits for 24616. Run 2, however, has six out of eight (75 percent) of the elements having values outside the control limits. This would suggest that Run 2 of 029-QC-2 is not representative of the sample and should be disregarded. With Run 2 omitted from the data, none of the elements in 029-QC-2 (average of Run 1 and Run 3) falls outside the control limits for 24616.

ESCA Accuracy

There are no standard reference materials for surface analysis with which to evaluate accuracy of the ESCA analytical technique. Therefore, blind duplicates of two of the test samples were submitted to the analysts for use as internal QC samples. They were as follows:

Label	Identity	Data Tables
029-QC-1	3610	11 (3610 Results, 6)
029-QC-2	24616	12 (24616 Results, 8)

The true identities of the samples were unknown to the analysts so that the accuracy of elemental identifications and quantification could be evaluated without analyst bias. This bias would be most apparent in the subjective portion of the analysis, distinguishing elemental photoelectron peaks from noise in the spectrum.

Problems with identification of elements in a sample are particularly apparent with 029-QC-1 (3610). Table 26 compares data for the sample and its blind duplicate. Note that sodium is detected in only one aliquot of the blind duplicate, but was quantified in all three of the original 3610 aliquots. In addition, the blind duplicate identified titanium and iron in single aliquots while the original sample did not detect either of these elements. Similar problems with identification occurred with the 029-QC-2 and 24616 duplicate pair. These data are presented in Tables 27 and 28. Table 27 contains data for triplicate analyses of 029-QC-2. Table 28 contains the data calculated from Run 1 and Run 3, because Run 2 was judged to be invalid.

TABLE 26. EVALUATION OF BLIND DUPLICATES BY ESCA (PERCENT ATOMIC)

	029-QC-1				3610
Element	Run 1	Run 2	Run 3	$\overline{X}$	Control Limits
Carbon	45	45	38	43	43 - 51
Oxygen	36.2	36.2	42.2	38.2	28.7 - 40.7
Calcium	3.3	3.0	3.4	3.2	2.0 - 3.8
Sodium	ND	0.6	ND	-	0.3 - 0.5
Sulfur	3.6	3.5	3	3.4	2.6 - 4.4
Silicon	5.0	5.0	5.5	5.2	4.3 - 5.9
Aluminum	6	6.6	6	6	6.0 - 6.2
Titanium[a]	0.9	ND	ND	-	ND
Iron[a]	ND	ND	1	-	ND

[a] Identification unconfirmed.

TABLE 27. EVALUATION OF BLIND DUPLICATES BY ESCA (PERCENT ATOMIC)

	029-QC-2				24616[a]
Element	Run 1	Run 2	Run 3	$\overline{X}$	Control Limits
Carbon	37	56.5	39	44	30 - 48
Oxygen	38.6	29.1	41.2	36.3	34.8 - 43.6
Calcium	9.2	5.5	9.7	8.1	8.0 - 9.6
Sodium	0.6	0.5	0.8	0.6	0.6 - 0.8
Sulfur	3.9	2	3.3	3	3.6 - 7.0
Silicon	2.6	1	1	2	0.8 - 3
Aluminum	4	3	2	3	_[b]
Chlorine	1	1	2	1	1.8 - 3.6
Phosphorus	3	1	ND	2[c]	0.8 - 3

[a] Data from first calculation on the spectra (Table 8).

[b] Aluminum was detected in only 1 out of the 3 aliquots used to establish control limits.

[c] Average of n=2 measurements.

TABLE 28. EVALUATION OF BLIND DUPLICATES BY ESCA (PERCENT ATOMIC)

	029-QC-2[a]			24616[b]
Element	Run 1	Run 3	$\overline{X}$	Control Limits
Carbon	37	39	38	30 - 48
Oxygen	38.6	41.2	39.9	34.8 - 43.6
Calcium	9.2	9.7	9.5	8.0 - 9.6
Sodium	0.6	0.8	0.7	0.6 - 0.8
Sulfur	3.9	3.3	3.6	3.6 - 7.0
Silicon	2.6	1	2	0.8 - 3
Aluminum	4	2	3	-[b]
Chlorine	1	2	2	1.8 - 3.6
Phosphorus	3	ND	-	0.8 - 3

[a] Run 2 deleted as nonrepresentative of the sample.

[b] Data from first calculation of the spectra (Table 9).

Quantification of elements detected in the samples seems to be more consistent than actual identification of low concentration elements. For the duplicate pair of 029-QC-1 and 3610, only two individual concentrations, carbon and oxygen in Run 3, fall outside the control limits for elements positively identified in all six aliquots (three original, plus three blind duplicates). The mean concentrations for the three blind aliquots all fall within the control limits. Indications are that the precision estimates generated for Sample 3610 are quite good and that the ESCA technique can quantitate elemental concentrations within the accuracy defined by the relative standard deviation.

Additional data obtained for Sample 24616 and its blind duplicate, 029-QC-2, show less consistent quantitative data, but better qualitative identifications. As discussed with precision determinations, 75 percent of the elemental quantifications for Run 2 of 029-QC-2 fall outside the control limits set by triplicate analyses of Sample 24616. If this aliquot is rejected as non-representative of the sample, the average concentrations of Run 1 and Run 3 all fall within the control limits (Table 28). Several individual values in these two runs do fall slightly outside the control limits, but overall, the data achieve the accuracy predicted by triplicate analyses of 24616.

Without standard reference materials to use for determining the accuracy of ESCA elemental analyses, it is impossible to make definitive statements on the technique's capabilities in that regard. For environmental samples, in which sample inhomogeneity is quite common, accuracy and precision are, to a great extent, limited by the samples themselves. In addition, samples such as were used in this study can significantly change in composition by adsorption of water and ambient air hydrocarbons. If surface oxygen and carbon are increased by this adsorption, the concentration of other elements such as silicon, sulfur, and various metals, will appear to decrease. For the characterization of pure substances; i.e., metal foils, argon ion etching can be used to remove such adsorbed contamination. However, combustion source particulates may have different surface and subsurface compositions because of the way they were formed, and argon ion etching may expose these subsurface layers rather than the particle surface. In addition, argon ion etching causes a scrambling of elemental oxidation states and can only be utilized after speciation studies have been completed.

For small grain size particulate samples in which problems of inhomogeneity can be somewhat minimized, relative accuracy within 30 percent can likely be achieved. Absolute accuracy cannot be determined without appropriate reference materials and will be dependent on condition of the sample and the analytical procedures used. An example of this is the estimated detection limit of chromium in the same sample when using different numbers of scans accumulated.

The spectra were evaluated in terms of noise level in the Cr2p binding energy range and analysis time. ESCA identifications, baseline estimates, and peak height measurements were performed manually and rely heavily on the experience and judgment of the analyst. Therefore, noise level was measured as the vertical range (in millimeters) about an average baseline estimated by eye. For five scans, the noise level was ± 2 mm, requiring that an observed signal be 4 mm in height (two times noise) to be measurable. For ten scans, the noise level was ± 1 mm resulting in a minimum measurable peak height of 2 mm. Correlating these peak heights to a concentration in the waste sample produced the data in Table 29.

Accumulating five scans takes 1.5 hours and ten scans take three hours. These data would suggest that by doubling the analysis time, one could double sensitivity at low levels. However, they represent analyses of two aliquots of the same sample for which both five scans and ten scans gave a Cr2p peak at the detection limit. Measured chromium concentrations are 1 percent atomic and 0.4 percent atomic, respectively. This variation in concentration suggests that quantification at or near the detection limit, as determined by background noise, is less than satisfactory and should be so noted.

Percent differences of the two sets of data are also presented in Table 29. It can be noted that low concentration elements show great discrepancy in both qualitative identifications and quantitation. The former can be attributed to mis-identification of noise as actual photoelectron signal, the latter to apparent variation in peak height that is, in fact, an improvement of the signal relative to noise level. Lead (Pb) concentrations show little difference because the Pb4f electrons have a high sensitivity and produce peaks greater than 30 mm at a 1.5 percent concentration. Chlorine falls in a region with a very low noise level above which its 4 mm peak height remained quite consistent. In summary, identification of low concentration elements suffers because of poor signal-to-noise ratio in the spectral region of the most sensitive peak for that element. In addition, minor differences in peak height above background, as measured by the analyst, cause more significant differences in the calculated concentration where peak heights are less than 5 to 10 mm.

METALS SPECIATION BY ESCA

Several metals were selected for speciation studies based on the needs of other groups researching particulate materials from hazardous waste incineration and based on metals of environmental significance which were quantified in the samples made available to this study. MRI was concerned about the possible oxidation of Cr(III) in a waste material to Cr(VI) in flyash and bottom ash produced by its incineration. Lead and zinc, which were found in several of the incinerator particulate samples (primarily the filter catches), would be expected to behave differently following environmental disposal depending on the compound form/oxidation states present. In addition, both are priority pollutant metals.

The general approach to speciation of these metals was to determine, from the literature, whether previous ESCA researchers had been able to distinguish various oxidation states of the element. Following positive indications from the literature, high purity compounds of the element(s) representing different oxidation states were obtained for use as standards. The initial search for such standards focussed on reagents available in-house and was followed by purchase from a chemical supplier when in-house supplies were insufficient. Major concerns regarding the choice of standard compounds included their

TABLE 29. COMPARISON OF MEASURED CONCENTRATIONS FOR NS=5 SCANS AND NS=10 SCANS

	Percent atomic		
Element	27747 ns=5	27747 ns=10	Percent difference
Carbon	85.1	85.9	0.9
Oxygen	8.8	11	25
Sulfur	1	ND	-
Chlorine	1	1	0
Lead	1.4	1.2	14
Zinc	ND	0.5	-
Titanium	0.8	ND	-
Chromium	1	0.4	60

ability to withstand the vacuum produced in the ESCA chamber without decomposition or sublimation and compiling a fairly comprehensive data base of common oxidation states.

Chromium Speciation

Quantification and speciation of chromium from hazardous waste incineration were studied to determine whether Cr^{+3} in a waste sample is oxidized to the more hazardous Cr^{+6} by the process and emitted with effluent particulate. Based on published research, it was believed to be quite easy to differentiate Cr^{+3} from Cr^{+6} using ESCA. Standards of Cr° (chromium metal), Cr^{+3} (chromium (III) oxide-Cr_2O_3), and Cr^{+6} (potassium chromate-K_2CrO_4) were purchased from Alfa Ventron, Danvers, Massachusetts. Aliquots were mounted on sintered steel and sticky tape substrates and analyzed by ESCA for carbon 1s, oxygen 1s, and chromium 2p photoelectrons. Following standard practice, the carbon 1s peak from hydrocarbons was taken as having a constant binding energy from one sample to the next. It was, therefore, possible to calculate energy shifts from carbon (ΔE C/Cr) for each chromium oxidation state and simultaneously to eliminate energy shifts associated with sample charging. These data are presented in Table 30.

TABLE 30. ENERGY SHIFTS OF CHROMIUM STANDARDS

Standard	Oxidation state	ΔE C/Cr
Chromium metal	Cr^{o}	292.0[a]
Cr_2O_3	Cr^{+3}	291.7[b]
K_2CrO_4	Cr^{+6}	294.3[b]

[a] Mean for n=6 measurements.

[b] Mean for n=2 measurements.

Results of chromium standards analyzed for this study concur with those previously published.[9] Although earlier workers used the Cr3p electrons rather than the Cr2p used here, shifts between species were of similar magnitude and were shown, except for chromium metal, to exhibit a trend of increased binding energy with increased charge. From these results, we anticipated success in determining chromium oxidation states.

To evaluate chromium speciation more fully, a mixture of the Cr^{+3} and Cr^{+6} standards was prepared by grinding the salts together and placing the sample on a sticky tape substrate. The mixture was analyzed for carbon 1s, oxygen 1s and chromium 2p electrons by ESCA. Figure 5 is a composite spectrum of the Cr2p electrons for the individual standards and the mixture. Note that

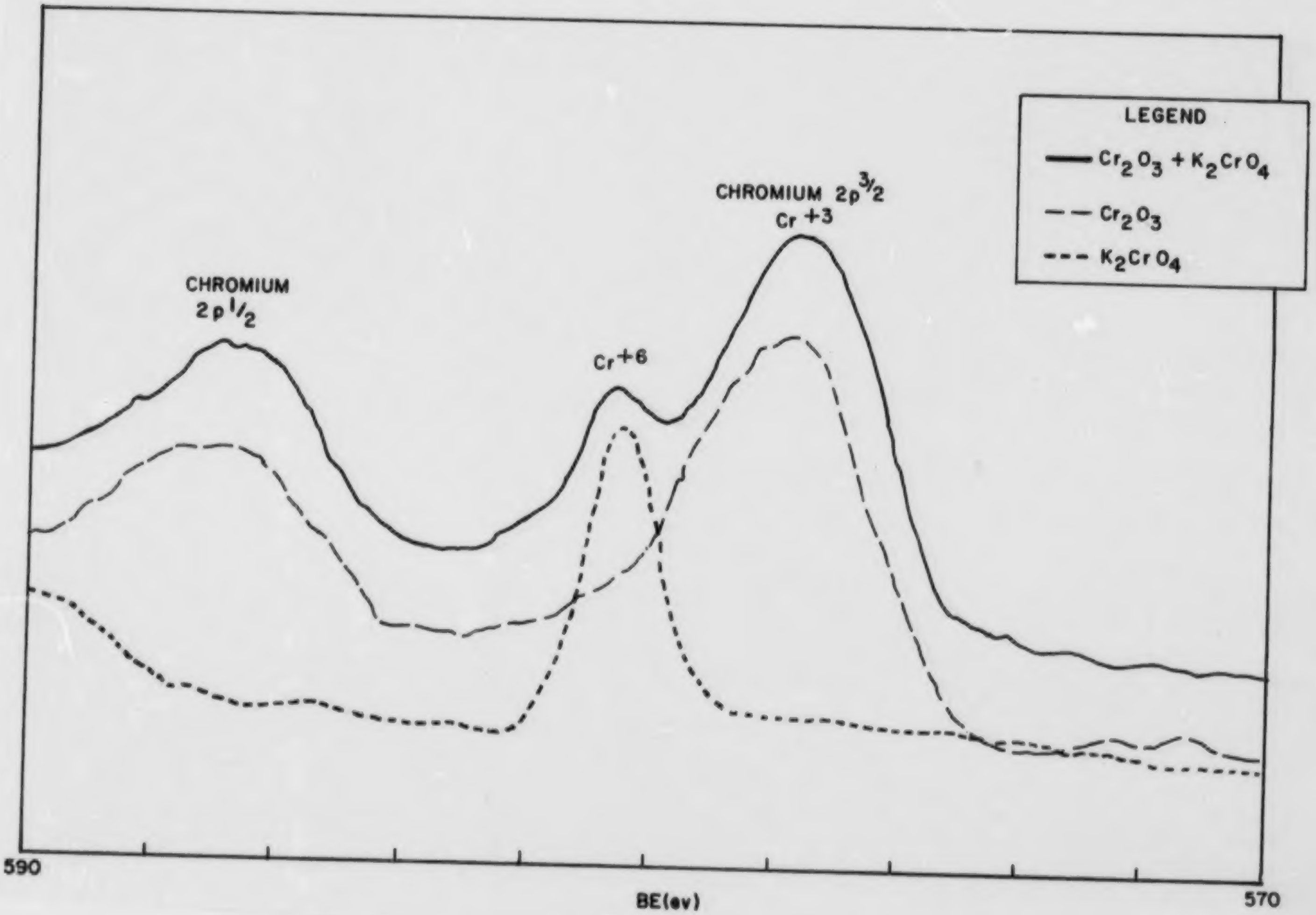


Figure 5. Speciation of chromium by ESCA.

these are actual spectra of the standards rather than computer-generated curves to match the spectrum of the mixture. In the figure, binding energy has been corrected for sample charging by setting the hydrocarbon C1s peak at 284.8 eV. As can be seen from the figure, the two chromium species can be easily identified in the mixture.

Subsequent to the ESCA analysis of chromium standards, source samples were obtained for study. Two of these were organic waste samples, GCA 27747 and 27748, containing 4700 μg/g and 700 μg/g of chromium, respectively. The other two, GCA 27745 and 27746, were stack particulates collected on Method 5 filters. No elemental composition data were available for the particulate samples, but they were known to have originated from the incineration of "mixed hazardous waste." The source samples were used to estimate the detection limit for chromium by ESCA as described above.

Chromium speciation was attempted on these and samples subsequently obtained for this study. However, none of the samples contained sufficient chromium to determine a precise binding energy for the Cr2p electron. A similar problem occurred when GCA 21369 and 21370 were analyzed and vanadium speciation was attempted. The obvious conclusion is that speciation cannot be performed when elements are present at or near their detection limit concentrations.

Lead Speciation

The species of lead present in a solid waste sample can be a significant factor in determining its behavior in a disposal situation. The leaching of lead from the solid into the aqueous phase would be unacceptable from an environmental health perspective. Therefore, if ESCA could be used to determine the oxidation state(s) of lead in the solid, it might be possible to predict the leachability hazard associated with that waste. From the literature,[10] it was determined that ESCA had been used to speciate elemental lead and several lead oxides. No data were available on lead salts.

Lead standard compounds were obtained from those available in-house; all were ACS reagent grade or better and were chosen to be compatible with vacuum conditions expected during ESCA analysis. Spectral scans were run of the carbon 1s and lead 4f photoelectrons for replicate aliquots of each compound. The mean difference in binding energy (ΔE C/Pb) between the C1s and Pb 4f7/2 was taken as the identifier of that lead species. Table 31 presents data for individual aliquots and calculated mean, standard deviation and percent RSD, as appropriate. Numerical precision on the measurements is excellent; however, the identification of single or multiple peaks present in the spectrum was less consistent. Literature values were not available with which to compare results for lead salts; this is particularly important for aliquots analyzed concurrently with Runs 2 and 3. Time did not permit reanalysis of these aliquots and an assumption was made that one of the standards, possible lead nitrate, decomposed somewhat under vacuum and contaminated those samples in nearby sample wheel positions. (The gold standard also showed minor lead contamination.)

TABLE 31. LEAD SPECIATION OF STANDARD COMPOUND

	ΔEC/Pb						
Compound	Run 1 (12/6/83)	Run 2 (1/18/83)	Run 3 (1/18/83)	$\overline{X}$	S	RSD (%)	Remarks
Pb (etched)	148.1	148.1	NA^3	148.1	-		
Pb (unetched)	147.0	146.6	146.7	146.8	0.2	0.1	Represents adsorbed PbO
Pb_3O_4	146.7	146.9	146.8	146.8	0.1	0.07	
PbO_2	147.2 146	147.5 146.4	147.4 146.7	147.4 146	0.2 0.4	0.1 0.3	Severe peak asymmetry^b
$PbSO_4$	145.4 -	145.2 146.4	145.2 146.6	145.3 146.5	0.1 -	0.07 -	Peak asymmetry for Runs 2 and 3
$PbCl_2$	145.9 -	145.8 147.0	145.4 -	145.7 -	0.3 -	0.2 -	Peak asymmetry for Run 2
$Pb(NO_3)_2$	NA	144.7 147.1	144.6 148.1	144.7 147.6	- -	- -	 Minor peak

[a] NA = Not analyzed.

[b] Peak asymmetry indicates the presence of multiple oxidation states with peaks unresolved.

Table 32 compares values obtained in this study with those from the literature. The elemental lead and PbO values are in good agreement. However, Pb_3O_4 and PbO_2 were significantly different, showing different numbers of peaks than would be expected. Initially, this was thought to be attributable to analyst error, but carefully repeated analyses produced virtually the same results for triplicate aliquots. The only explanation that can be offered is that the reagents used as standards had suffered some degradation during storage. When the lead oxidation state study was initiated, it was intended to conduct a quick study to determine whether the literature values could be reproduced. It did not seem necessary to purchase fresh standards for this comparative study. It has since been learned, however, that lead oxides degrade sequentially from PbO_2 to Pb_3O_4 to PbO with evolution of O_2 at each step.[11] Such degradation would be particularly apparent in the surface regions of the powder, exactly where ESCA analyzes. The step-wise degradation would be consistent with our findings.

Because of this mixing of oxidation states for the oxides, it was decided that lead oxidation state studies should restrict identification of unknowns to three classes; i.e., metal, lead oxides, and lead salts, rather than attempting to identify individual compounds. Table 33 presents oxidation state data for lead in particulate filter samples from waste incineration. Note that these data are for before and after aqueous leaching. Based on these results, one would conclude that lead in Samples 27745 and 27746 most closely resembles lead salts in electron binding energy. The lead in Sample 29174 has a binding energy somewhat closer to that of an oxide, but this would be a questionable identification. Only minor differences in binding energy, on the order of instrument resolution (0.2 eV), were observed before and after leaching. This would suggest that leaching; i.e., exposure to water, did not change the compound forms of lead. Further discussion on lead species believed to be present in these samples is presented elsewhere in Section 6.

Zinc Speciation

Much like lead, zinc is a priority pollutant metal whose leaching from incinerator ash could present a hazardous waste disposal problem. In a brief literature review, no references were found to indicate that ESCA could be used to speciate zinc. Therefore, several zinc compounds were chosen from in-house stores to permit a quick study of the element's binding energy shifts. The energy differences (ΔE C/Zn) were measured from the carbon 1s to the Zn3p photoelectrons. These data are presented in Table 34. Note that essentially replicate values for Zn^0 and ZnO were obtained by analyzing a zinc metal sample before and after argon ion etching. This etching would remove surface oxides and expose more of the elemental zinc characteristic of the bulk. The average of the two "runs" was used as the identifier of the species. $ZnCl_2$ was only analyzed once.

The fairly large binding energy shifts associated with the three species suggest that it should be quite easy to distinguish the species in incinerator particulate samples. Data for the two samples which contained quantifiable amounts of zinc are presented in Table 35. Both showed fairly low electron counts (40 counts/sec) above background with each spectrum shifted

TABLE 32. COMPARISON OF EXPERIMENTAL AND LITERATURE VALUES FOR LEAD SPECIATION

Compound	ΔEC/Pb Experimental[a]	ΔEC/Pb Literature[b]	Remarks
Pb (etched)	148.1	NA[c]	
Pb (unetched)	146.8	147.2	Represents adsorbed PbO
PbO crystalline	NA	146.9	
Pb_3O_4	146.8	146.9 145.9	
PbO_2	147.4 146.4	147.3 NA	
$PbSO_4$	145.3	NA	
$PbCl_2$	145.7	NA	
$Pb(NO_3)_2$	144.7	NA	

[a] Spurious values for Pb salts analyzed during same analysis series have been eliminated from this tabulation.

[b] Literature values obtained from Kim, T. S., et al. (Ref. 10) based on typical C_{1s} binding energy set at 284.8 eV.

[c] NA = Not available.

TABLE 33. LEAD SPECIATION IN INCINERATOR PARTICULATES

Before leaching		After leaching	
Sample	ΔEC/Pb	Sample	ΔEC/Pb
27745-1	145.8	27745-L1	145.8
27745-2	145.9	27745-L2	145.7
27746-1	145.9	27746-L1	145.5
27746-2	145.7	27746-L2	NA
29174-1	146.2	29174-L1	146.1
29174-2	146.3	29174-L2	146.1
29174-3	146.3		

TABLE 34. ZINC SPECIATION OF STANDARD COMPOUNDS

Compound	Run 1[a]	Run 2[a]	ΔEC/Zn
Zn metal	195.8	196.0	195.9[b]
ZnO (adsorbed)	193.4	193.3	193.4[b]
$ZnCl_2$	-	-	194.4

[a] Two values for Zn^o and ZnO were obtained by analyzing the same zinc metal standard before and after argon ion etching. Two species could be distinguished in each.

[b] Average of Run 1 and Run 2.

approximately 2 eV toward higher binding energy, perhaps caused by slight sample charging. The ΔE C/Zn values reported for the unknowns fall intermediate to those for Zn^o and $ZnCl_2$. One possible explanation is that a mixture of the two species is present which could not be resolved by the instrument. However, examination of the full width at half maximum (FWHM) of the peak heights for samples and the standards, particularly $ZnCl_2$, revealed only slight broadening of the sample peak widths when compared to the standard (less than 5 percent greater). Such a small difference could be the result of experimental error. An alternative explanation, and one considered more plausible, is that the zinc is in the form of an ionic compound other than the chloride. This would explain the shift in binding energy from $ZnCl_2$ and would not contradict the findings of a peak shape comparison. The samples and the $ZnCl_2$ standard have very similar compound forms of zinc. An identification of the samples as containing ionic zinc other than the chloride would be compatible with all the available data. The data are not sufficient, however, to state this with certainty.

TABLE 35. ZINC SPECIATION IN INCINERATOR PARTICULATE

Before leaching		After leaching	
Sample	ΔEC/Zn	Sample	ΔEC/Zn
27745-1	195.2	27745-L1	195.0
27745-2	195.1	27745-L2	195.2
27746-1	195.1	27746-L1	194.9
27746-2	195.2	27746-L2	NA[a]

[a] NA = Not analyzed.

ANALYSIS OF LEACHATE SOLUTIONS

Leachate solutions were analyzed for anions by ion chromatography (IC) and for metals by inductively coupled plasma emission spectroscopy (ICP). These data are presented in Tables 36 through 43 and Tables 44 through 49, respectively. The primary purpose in obtaining these data was to corroborate the findings of ESCA analysis of the samples before and after leaching. In addition, it was hoped that precision of leachate generation and solution analysis could be estimated.

Triplicate leachate generations and analyses were conducted only for samples 3610, 9949 and 24616. IC data for these samples shows 3610, a fine particulate, to be reproducibly extracted and analyzed within the expected relative standard deviation (± 15 percent). Results for 24616 were unexpectedly poor with sulfate having 52 percent RSD and chloride having

TABLE 36. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 3610)

Element	Aliquot 1	Aliquot 2	Aliquot 3	$\overline{X}$	S	RSD (%)	Control Limits
Sulfate	1690	1570	1890	1720	162	9.4	1400 - 2040
Chloride	52.5	57.5	65.0	58.3	6.3	11	45.7 - 70.9
Fluoride	1.1	0.9	1.0	1.0	0.1	10	0.8 - 1.2
Nitrate	ND	ND	ND	ND	-	-	-

TABLE 37. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 9949)

Element	Aliquot 1	Aliquot 2	Aliquot 3	$\overline{X}$	S	RSD (%)	Control Limits
Sulfate	243	140	105	163	72	44	19 - 307
Chloride	ND	ND	ND	ND	-	-	-
Fluoride	ND	ND	ND	ND	-	-	-
Nitrate	ND	ND	ND	ND	-	-	-

TABLE 38. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 24616)

Element	Aliquot 1	Aliquot 2	Aliquot 3	$\overline{X}$	S	RSD (%)	Control Limits
Sulfate	297	96.2	190	194	100	52	DL[a] - 394
Chloride	1350	1820	260	1140	800	70	DL - 2740
Fluoride	3.2	3.0	3.1	3.1	0.1	3.2	2.9 - 3.3
Nitrate	367	311	332	337	28	8.3	281 - 393

[a] DL = detection limit.

TABLE 39. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 029-QC-1, BLIND DUPLICATE OF SAMPLE 3610)

Element	Aliquot 1
Sulfate	2000
Chloride	56.0
Fluoride	1.1
Nitrate	ND

TABLE 40. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 029-QC-2, BLIND DUPLICATE OF SAMPLE 24616)

Element	Aliquot 1
Sulfate	94.0
Chloride	2140
Fluoride	3.1
Nitrate	349

TABLE 41. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 27745)

Element	Aliquot 1
Sulfate	11.2
Chloride	38.2
Fluoride	0.3

TABLE 42. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 27746)

Element	Aliquot 1
Sulfate	122
Chloride	645
Fluoride	2.4
Bromide	20

TABLE 43. IC RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 29174)

Element	Aliquot 1
Sulfate	52.4
Chloride	3.9
Fluoride	ND
Bromide	20

TABLE 44. ICP RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 3610)

Element	Aliquot 1	Aliquot 2	Aliquot 3	$\overline{X}$	S	RSD (%)	Control Limits
Calcium	728	732	654	705	43.9	6.2	617 - 793
Sodium	24.3	23.5	30.2	26.0	3.7	14	18.6 - 33.4
Silicon	<5	<5	<5	<5	-	-	-

TABLE 45. ICP RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 9949)

Element	Aliquot 1	Aliquot 2	Aliquot 3	$\overline{X}$	S	RSD (%)	Control Limits
Calcium	83.2	40.5	36.3	53.3	26	49	1.3 - 105
Sodium	1.9	1.9	1.1	1.6	0.5	31	0.6 - 2.6
Silicon	<5	<5	<5	<5	-	-	-

TABLE 46. ICP RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 24616)

Element	Aliquot 1	Aliquot 2	Aliquot 3	$\overline{X}$	S	RSD (%)	Control Limits
Calcium	1510	1340	1480	1440	91	6.3	1260 - 1620
Sodium	799	807	784	797	12	1.5	773 - 821
Silicon	<5	<5	<5	<5	-	-	-

TABLE 47. ICP RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE SRM 1633a)

Element	Aliquot 1
Calcium	269
Sodium	15.4
Silicon	<5

TABLE 48. ICP RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 029-QC-1, BLIND DUPLICATE OF SAMPLE 3610)

Element	Aliquot 1
Calcium	721
Sodium	26.4
Silicon	<5

TABLE 49. ICP RESULTS (μg/ml) OF LEACHATE ANALYSIS (SAMPLE 029-QC-2, BLIND DUPLICATE OF SAMPLE 24616)

Element	Aliquot 1
Calcium	1310
Sodium	418
Silicon	<5

70 percent RSD. Such scattered results were not obtained for fluoride and nitrate in the sample which were both less than 10 percent RSD. Neither was there a pattern to the extraction efficiency in the individual aliquots. No adequate explanation can be found for these data because the aqueous leaching procedure itself has been found to demonstrate good precision for anions in similar sample matrices (±15 percent RSD).[12] Sample 9949, a large particle size sample, showed (not surprisingly) 44 percent RSD for sulfate extraction and analysis. This could be attributed partially to the inhomogeneity encountered with larger particle sizes, but also to the species of sulfur encountered on this sample. Sample 9949 is a sulfur recovery ash which typically contains a mixture of sulfate and sulfide. It is likely that sulfates would be fairly efficiently extracted from the sample surface and that sulfide would only slowly oxidize, if at all. The amount of sulfate extracted from the sample would depend on the amount of sulfate present and the amount of exposed surface area of the particulate. The problem of inhomogeneity with large particles was also apparent in the ESCA results.

The blind duplicate samples submitted for ESCA analysis also serve as internal QC checks for leachate analyses. Sample 029-QC-1, which is a duplicate of 3610, falls within the control limits (for that sample) for all anions quantified. These results were quite encouraging, given the fairly tight precision obtained for 3610. Sample 029-QC-2, the duplicate of 24616, also fell within the control limits for that sample; however, it seems of little significance in light of the 50 to 70 percent RSD for two of the anions.

ICP analyses of leachates generated by the aqueous extraction procedure fared somewhat better than ion chromatography. Again, with the exception of 9949, ICP results were within 15 percent RSD for elements quantified in the leachate. These elements were restricted to those detectable by ESCA which, for 3610, 9949, and 24616, were calcium, sodium and silicon. Sample 9949 showed its usual unpredictability with 30 to 50 percent RSD. Again, this can best be attributed to inhomogeneity being significant for large particle size samples.

Sample 029-QC-1 fell within the control limits for Sample 3610 for all three elements. Sample 029-QC-2, however, was far below the expected concentration range for sodium in 24616. Again, no explanation can be offered for this spurious value. Sample preparation sheets were checked to determine whether significant differences existed in aliquot size or final volume of leachate, but none were found. Even extending the control limits to the worst case expected for the aqueous leaching procedure (15 percent RSD) only gave a lower control limit of 557, not sufficient to bring the 029-QC-2 sodium concentration into control.

No ICP data were obtained for leachates of Samples 27745, 27746, or 29174. Aliquots of these solutions were not properly preserved for metals analysis and no additional attempts were made to recover these solutions. Although this at first seemed a serious loss to the program, considering that these samples contained greater numbers of trace metals than the first series analyzed, an examination of ESCA data before and after leaching suggested that few metals would have been found in the leachate. This is corroborated by an evaluation of the aqueous leaching procedure[12] which found less than 2 percent extraction efficiency for metals in similar matrices.

ESCA BEFORE AND AFTER LEACHING

Tables 50 through 56 compare elemental concentration data obtained by ESCA analyses performed before and after aqueous leaching. The concentration values reported are the average of replicate analyses for that sample that were judged to be valid data; i.e., that were representative of the sample and did not indicate substrate breakthrough. The third column on each table indicates whether the concentration of the elements significantly increased or decreased as a result of leaching. This determination is somewhat subjective in that a decision must be made as to whether the change in concentration is real or merely the result of analytical variation. Generally, a change of greater than 10 or 15 percent was judged to be an actual change in sample composition and was so noted in the tables. These values were chosen as average precision capabilities for replicate analyses. Although much greater variation was found in several of the particulate samples, using precision guidelines of greater than 20 percent could mask many real changes in sample concentration. In addition, anion and metals data from the leachates is used to corroborate the findings by ESCA.

For the most part, samples showed an increase in oxygen after leaching that was attributed to adsorbed water. Despite oven drying at 104°C for 12 hours, some water remained in samples that had been leached. As a result, the apparent carbon concentration usually decreased, most likely the result of masking by other elements. It must be remembered that concentrations calculated by ESCA are relative percentages, not absolute concentrations. Therefore, an increase in one element results in an apparent decrease in the other elements. This makes supporting chemical data from leachate analysis particularly important in an experimental program such as this.

Elements for which chemical data are available include calcium, sodium and silicon by ICP and sulfur, chlorine, fluorine, and nitrogen by IC. The tables comparing ESCA data also include the concentrations of the elements in the leachate reported as μg/ml of the ion (sulfate, nitrate) when appropriate. These concentrations are used as qualitative or, at best, semi-quantitative indicators of elements leached from the particulate matter. A final column notes whether the ESCA and leachate data are in agreement.

The ESCA/leachate data indicates that much of the particulate matter associated with process wastes consists of a core of aluminosilicates, fluidized bed or caustic scrubber material and low solubility trace metals. These often serve as condensation nuclei for species, such as HCl and H_2SO_4, generated during combustion which then adsorb onto particulate matter as the gas cools. Similar phenomena have been seen in various combustion source particulate[13], but these rarely contain the metals content associated with the waste incineration samples used in this study. It is particularly interesting to note that lead and zinc appear to be present in the samples as ionic compounds, both before and after leaching. These two metals occur in compound forms which may volatilize at incineration temperatures.[14] Among these are Zn, $ZnCl_2$, $PbCl_2$, and possibly PbO. The lead oxide will very quickly condense upon cooling of combustion gases. Most of these metals condense out with wet scrubbing and could be captured with particulate fines from a caustic scrubber. This scenario would agree well with the data obtained in this study.

TABLE 50. COMPARISON OF ELEMENTAL COMPOSITION BEFORE AND AFTER LEACHING (SAMPLE 3610)

Element	Percent Atomic Before (ave, n=3)	 After (ave, n=2)	Change	Leachate analysis[a]	Remarks
Carbon	47	42	-		
Oxygen	34.7	42.4	↑		Adsorbed water
Calcium	2.9	4.0	↑	705	Acceptable
Sodium	0.4	ND	↓	26	Agrees
Sulfur	3.5	0.9	↓	1720	Agrees
Silicon	5.1	5.9	↑	<5	Agrees
Aluminum	6.1	5	-	NA[b]	

[a] Also detected in the leachate were chloride at 58 ppm and fluoride at 1 ppm.

[b] NA = Not analyzed.

TABLE 51. COMPARISON OF ELEMENTAL COMPOSITION BEFORE AND AFTER LEACHING (SAMPLE 9949)

Element	Percent Atomic Before (ave, n=3)	 After (ave, n=1)	Change	Leachate analysis[a]	Remarks
Carbon	79.8	44	↓		
Oxygen	13	42	↑		Adsorbed water
Sulfur	2.7	3	-	163	Acceptable
Silicon	1.4	ND	↓	<5	Agrees
Aluminum	4	5	-	NA[b]	
Iron	ND	6.0	↑	NA	

[a] Also detected in the leachate were calcium = 53.3 ppm and sodium = 1.6 ppm.

[b] NA = Not analyzed.

TABLE 52. COMPARISON OF ELEMENTAL COMPOSITION BEFORE AND AFTER LEACHING (SAMPLE 24616)

	Percent Atomic				
Element	Before (ave, n=3)	After (ave, n=2)	Change	Leachate analysis[a]	Remarks
Carbon	39	27	↓		
Oxygen	39.2	52.0	↑		Adsorbed water
Calcium	8.8	4.2	↓	1440	Agrees
Sodium	0.7	0.7	–	797	Acceptable
Sulfur	5.3	Trace	↓	194	Agrees
Silicon	2	4.3	↑	<5	Agrees
Aluminum	ND	9	↑	NA[b]	
Chlorine	2.7	0.9	↓	1140	Agrees
Phosphorus	2	2	–	NA	

[a] Also detected were fluoride = 3.1 ppm and nitrate = 337 ppm.

[b] NA = Not analyzed.

TABLE 53. COMPARISON OF ELEMENTAL COMPOSITION BEFORE AND AFTER LEACHING (SAMPLE 27745)

	Percent Atomic				
Element	Before (ave, n=2)	After (ave, n=2)	Change[a]	Leachate analysis	Remarks
Carbon	25	24	-		
Oxygen	39.7	53	↑		Adsorbed water
Calcium	6.3	ND	↓	NA[b]	
Sulfur	3	ND	↓	11.2	Agrees
Silicon	2.6	5	↑	NA	
Chorine	9.3	2	↓	38.2	Agrees
Phosphorus	5.8	7	-	NA	
Fluorine	2	ND	↓	0.3	Agrees
Lead	1.4	4.5	↑	NA	
Zinc	4.0	4	-	NA	
Tin	0.3[c]	0.4[d]			
Vanadium	0.9[c]	ND			

[a] Judgment not made for questionable identifications.

[b] NA = Not analyzed.

[c] Identification unconfirmed.

[d] Not detected in one aliquot but quantified at 0.7 percent in the other.

TABLE 54. COMPARISON OF ELEMENTAL COMPOSITION BEFORE AND AFTER LEACHING (SAMPLE 27746)

	Percent Atomic				
Element	Before (ave, n=1)	After (ave, n=1)	Change	Leachate analysis[a]	Remarks
Carbon	29	18	↓		
Oxygen	41.6	59.6	↑		Absorbed water
Calcium	4.1	ND[b]	↓	NA[c]	
Sulfur	3.8	ND	↓	122	Agrees
Silicon	3.5	7.5	↑	NA	
Chlorine	9.1	2	↓	645	Agrees
Phosphorus	4.7	7.1	↑	NA	
Fluorine	1	ND		2.4	Acceptable
Lead	2	3	↑		
Tin	0.3	ND			
Titanium	0.9	ND			
Iron	ND	1.4			
Potassium	ND	1			

[a] Also detected was bromide = 20 ppm.

[b] ND = Not detected.

[c] NA = Not analyzed.

TABLE 55. COMPARISON OF ELEMENTAL COMPOSITION BEFORE AND AFTER LEACHING (SAMPLE 27746)

Element	Percent Atomic				
	Before (ave, n=1)	After (ave, n=1)	Change	Leachate analysis[a]	Remarks
Carbon					
hydrocarbon	16	17	–		
other	14	4	↓		Carbonate dissolved
Oxygen	41	51	↑		Adsorbed water
Calcium	ND	1[c]		NA[d]	
Sodium	1	0.6	↓	NA	
Silicon	7.4	8	–	NA	
Chlorine	3	2	↓	3.9	Agrees
Phosphorus	2	4	↑	NA	
Lead	1.8	4.4	↑	NA	
Tin	3.7	4.0	–	NA	
Iron	ND	2	↑	NA	
Chromium	1	1	–		
Copper	5.1	ND	↓		
Potassium	4.1	ND	↓		

[a] Applies only to the aliquot which showed two carbon species.

[b] Also detected was sulfate = 52.4 ppm.

[c] Identification unconfirmed.

[d] NA = Not analyzed.

TABLE 56. COMPARISON OF ELEMENTAL COMPOSITION BEFORE AND AFTER LEACHING (SAMPLE 29174[a])

	Percent Atomic				
Element	Before (ave, n=2)	After (ave, n=1)	Change	Leachate analysis[b]	Remarks
Carbon	16	19	–		
Oxygen	52	55	–		
Calcium	ND	ND	–	NA[c]	
Sodium	2	0.8	↓	NA	
Silicon	9.4	9.0	–	NA	
Chlorine	2	ND	↓	3.9	Agrees
Phosphorus	3	4	↑	NA	
Lead	2.2	4.5	↑	NA	
Tin	4.4	4.0	–	NA	
Iron	1.5[d]	2		NA	
Chromium	1	2	↑		
Copper	1.5[d]	ND			
Potassium	4.9	ND	↑		

[a] Applies only to aliquots showing only one species of carbon.

[b] Also detected was sulfate = 52.4 ppm.

[c] NA = Not analyzed.

[d] One aliquot showed 3 percent of this element while the other aliquot reported not detected.

The species most easily leached from these samples were those that are formed in caustic scrubbers, the sodium and calcium salts of chloride, fluoride and sulfate. In addition, any residual acids of these anions would also have adsorbed on particulate surfaces and would easily be leached by the aqueous solution. For the most part, the metals present in the sample are of sufficiently low volatility to be among the first species to condense out from the vapor phase, perhaps even before the scrubber. In addition, they are usually of low aqueous solubility, particularly in caustic solution, and would not be leached, to any great extent, by the non-vigorous Level 1 procedure. Many of these conclusions could have been reached from a consideration of the behavior of various elements under combustion conditions rather than from the data obtained in this study. In fact, such a perspective was required to interpret the data obtained. It is encouraging, however, that the results seem to be in agreement.

REFERENCES

1. Siegbahn, K., et al. ESCA: Atomic, Molecular, and Solid State Structure Studied by means of Electron Spectroscopy. Almquist and Wiksells Boktryckeri AB. Uppsala, Sweden. 1967.
2. Berthou, H., and C. K. Jorgensen. Relative Photoelectron Signal Intensities Obtained with a Magnesium X-ray Source. Anal. Chem. 47, 482. 1975.
3. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA-600/7-78-201. U.S. Environmental Protection Agency, Research Triangle Park, N.C. 1978.
4. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. Document No. QAMS-005/80. U.S. Environmental Protection Agency, Washington, D.C. 1980.
5. Inductively Coupled Plasma -- Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes. Method 200.7. U.S. Environmental Protection Agency, Cincinnati, OH.
6. The Inductivety Coupled Argon Plasma Atom Comp, Jarrell-Ash Division/ Fisher Scientific Co., Waltham, Massachusetts.
7. GCA Analytical Laboratory Procedures Manual: Volume 1, Inorganic Analysis. 1982.
8. Hercules, D. M., Anal. Chem. 50, 734A. 1978.
9. Hendrickson, D. N., et al. Core Electron Binding Energies for Compounds of Boron, Carbon, and Chromium. Inorg. Chem. 9, 612. 1970.
10. Kim, T. S., et al. X-ray Photoelectron Spectra of Lead Oxides, Anal. Chem. 45, 2214. 1973.
11. Latimer, W. M., and J. H. Hildebrand. Reference Book of Inorganic Chemistry, Third Edition. The Macmillan Company, New York. 1951.
12. Bause, D. E. and K. T. McGregor. Comparison of Four Leachate Generation Procedures for Solid Waste Characterization in Environmental Assessment Programs. U.S. EPA Report No. EPA-600/7-80-118. May 1980.

13. Werner, A. S., et al. Preliminary Environmental Assessment of the Lignite-Fired CAFB. U.S. EPA Report No. EPA-600/7-79-048. February 1979.

14. Gerstle, R. W., and D. N. Albrinck. Atmospheric Emissions of Metals from Sewage Sludge Incineration. JAPCA 32, 1119. 1982.

APPENDIX A

QA AUDIT

GCA Technology Division

213 Burlington Road
Bedford, Mass. 01730
(617) 275-5444

To: 1-386-029 File

Date: 26 September 1983

From: R. M. Ellersick

Subject: QA Audit - ESCA and Leachate Analytical Procedures to Characterize Wastes in Process Streams

An audit of this project was conducted on 23 and 26 September 1983 to check on adherence to the QA Project Plan. The audit focused on the ESCA analytical work but the Ion Chromatograph (IC) and Inductively Coupled Argon Plasma (ICAP) work was checked for performance of stated QC measures.

Monthly reports and the Task Manager's project files were reviewed. The monthly reports gave brief summaries of the initial ESCA work and stated the need for samples with higher-level elemental concentrations. Monthly reports after such samples were provided presented detailed discussions of the chromium and lead speciation work undertaken; tables of results were included. The Task Manager's files were well-organized and appeared complete. A large ring-binder contained all ESCA spectra and it was easy to check from this raw data through data report and summary tables.

The project description given in Section 1 of the QA Plan was followed; samples were analyzed by ESCA before and after leaching and the leachates were analyzed by IC and ICAP. GCA did not collect any samples specifically for this task but those analyzed were logged in the Sample Bank Master Log and identified by GCA Control Numbers. Laboratory custody procedures were followed.

Instrument logs and raw data were checked for implementation of the calibration and internal QC procedures stated in the OA Plan. The results of this checking are noted below.

ESCA

Stated - Monthly calibration with gold foil to set machine function constant and verify analytical sensitivity. Monthly check of binding energy scale for speciation studies. Each substrate type used analyzed before start of analytical program. NBS SRM 1633a used as a QC sample; project samples analyzed in triplicate.

Actual - Machine function constant was checked monthly; gold and silver standards were run with every set of speciation study samples in addition to lead and chromium standard compounds. Sintered steel and sticky tape substrates were analyzed several times before project samples were analyzed. NBS SRM 1633a was run with every analysis set except the speciation studies. Triplicate aliquots were analyzed unless limited sample size prevented this.

IC

Stated - 3 point calibration curve run weekly; checked daily with a known QC sample, must agree within 5% of known value. Reagent blank run with each analysis batch; samples analyzed in triplicate.

Actual - 5 point curves were run for each compound on each analysis day; QC check samples agreed within 5%. A method blank carried through the leachate generation was run in addition to reagent blanks. Leachates from triplicate sample aliquots were analyzed.

ICAP

Stated - Instrument calibrated daily; checked with known QC sample to ± 5% of known value. Reagent blank included in each analysis batch; project samples run in triplicate.

Actual - Instrument was calibrated twice daily; QC check sample agreed with known values to within 5%. A leachate method blank was analyzed in addition to reagent blanks at all sample dilutions. Triplicate aliquots were leached and analyzed.

The analytical procedures were essentially followed as written in the QA Plan. Minor deviations from the leachate generation procedure were followed consistently for all project samples and will be noted in the Final Report. The formulas given on page 27 of the OA Plan were modified slightly in calculating ESCA analytical results; a factor was uniformly applied to eliminate decimal fractions.

The QA Plan states that NBS SRM 1633 or 1648 would be used as blind QC samples for performance audits. However, these samples are not certified for surface composition and no other reference materials suitable for auditing the accuracy of ESCA determinations were available. Therefore, no audit of ESCA accuracy was performed. The draft final report will present results of blind QC samples and interlaboratory studies which served to audit the other analytical work. Precision can be estimated for all techniques from the analysis results for replicate sample aliquots and for the blind duplicate aliquots of two project samples.

No Corrective Action Forms were initiated on this task; the fairly extensive ESCA substrate study was an immediate corrective action and was properly documented. The QA Plan is not consistent in its statements on reporting analytical data. Page 4 states all data including QA/QC results will be presented in the draft final report; page 41 states each monthly progress report will contain a QC section. Monthly progress reports have presented only small amounts of analytical data and have not included a QC section. The draft final report will include all analytical and QC data.

In summary, the audit of this project showed that the QC measures presented in the QA Plan were implemented. In many cases, more rigorous QC procedures were followed and clearly documented in laboratory notebooks and instrument logs. The raw data attests to conscientious analytical work by the entire project team.

RoseMary Ellersick

RoseMary Ellersick

RME/cf

cc: M.L. Atkinson
T.R. Copeland
B.M. Myatt
L.M. Seale
D.A. Stern

APPENDIX B

BROADBAND SPECTRA FOR ELEMENTAL QUANTIFICATION

Page

SUBSTRATE STUDY

Sample 3610 on Stainless Steel 74
Sample 3610 on Sticky Tape 75
Sample SRM 1633a on Stainless Steel 76
Sample SRM 1633a on Sticky Tape 77

ESCA BEFORE LEACHING

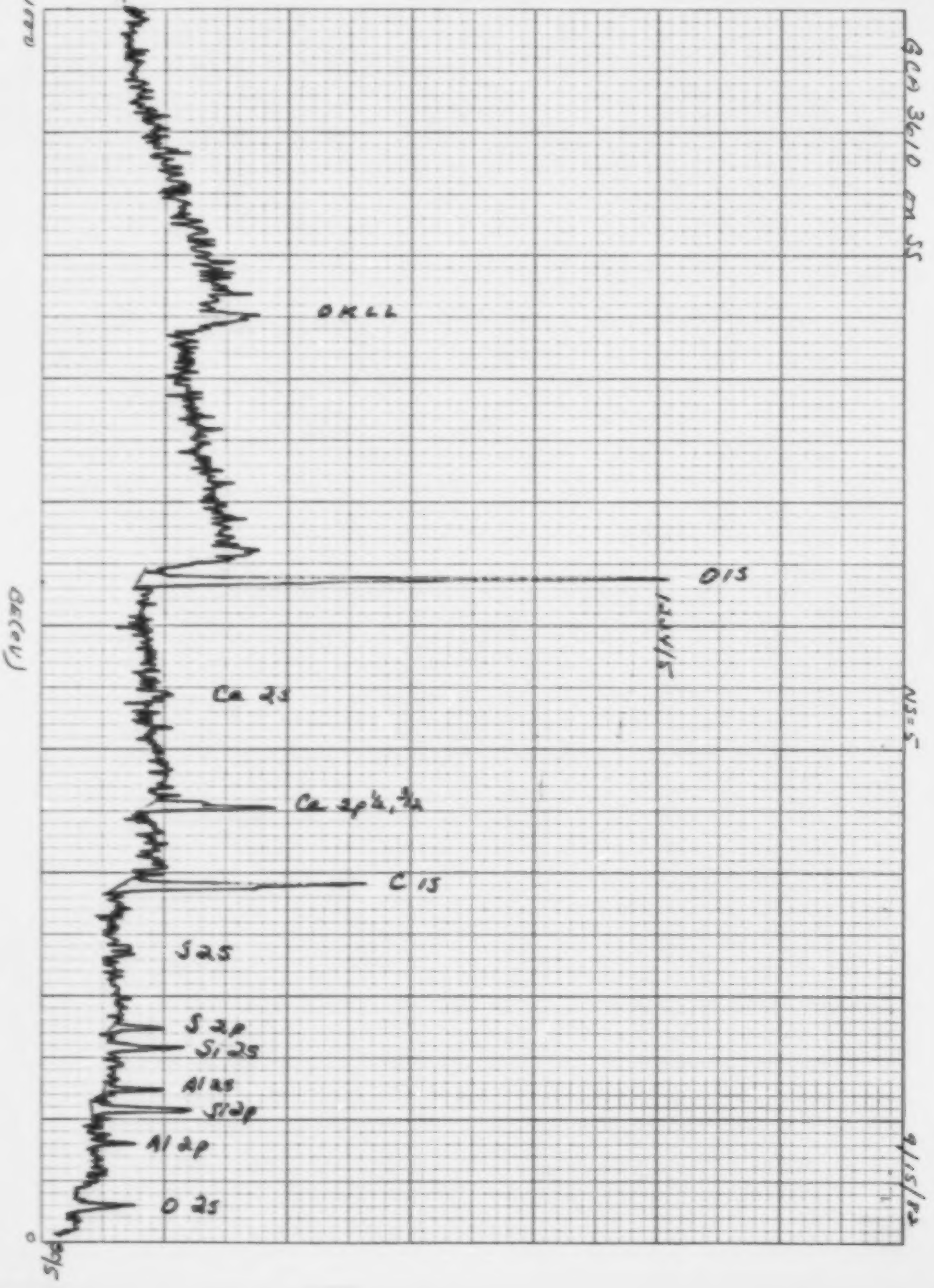
Sample 3610-1, NS = 5, 09/23/82 78
Sample 3610-2, NS = 5, 10/04/82 79
Sample 3610-3, NS = 5, 10/04/82 80
Sample 9949-1, NS = 5, 09/23/82 81
Sample 9949-2, NS = 5, 10/04/82 82
Sample 9949-2, NS = 10, 10/05/82 83
Sample 9949-3, NS = 5, 10/04/82 84
Sample 9949-3, NS = 5, 10/26/82 85
Sample 24616-1, NS = 5, 09/23/82 86
Sample 24616-2, NS = 5, 09/23/82 87
Sample 24616-3, NS = 5, 10/04/82 88
Sample 1633a-1, NS = 5, 09/23/82 89
Sample 1633a-2, NS = 5, 09/23/82 90
Sample 1633a-3, NS = 5, 10/04/82 91
Sample 029-QC-1-1, NS = 5, 09/23/82 92
Sample 029-QC-1-1, NS = 5, 10/04/82 93
Sample 029-QC-1-3, NS = 5, 10/26/82 94
Sample 029-QC-2-1, NS = 5, 09/23/82 95

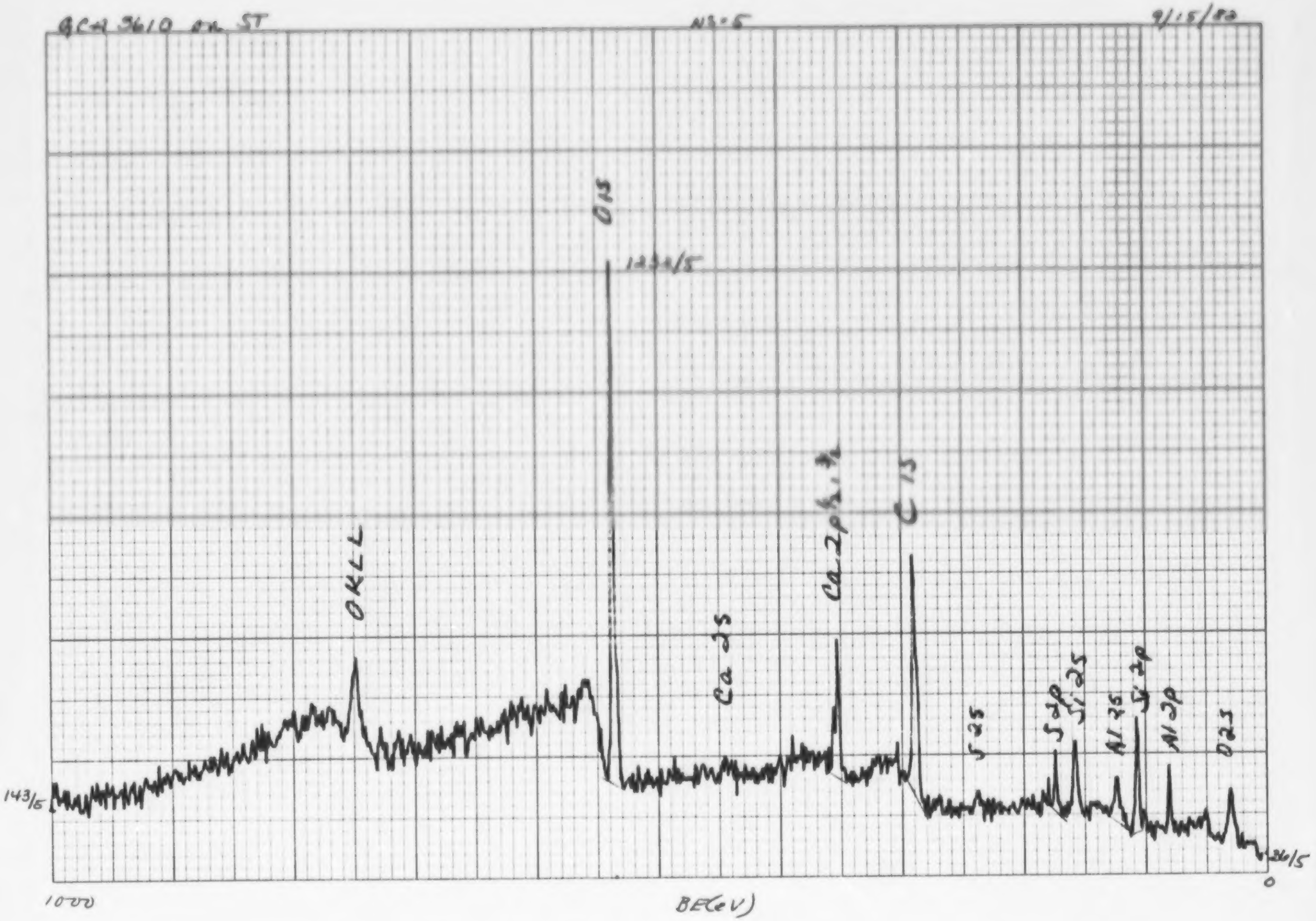
Page

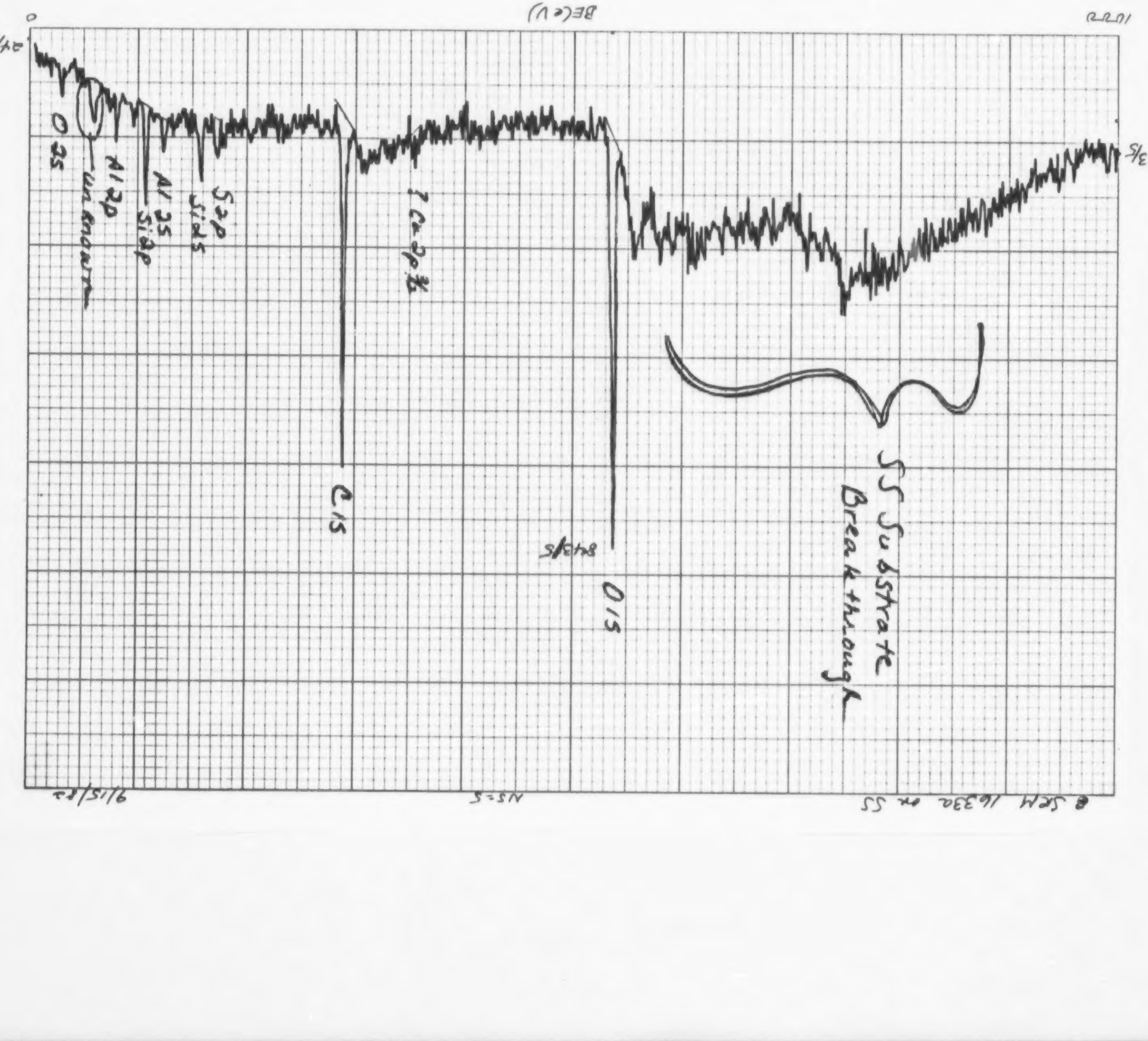
Sample 029-QC-2-2, NS = 5, 10/05/82 96
Sample 029-QC-2-3, NS = 5, 10/26/82 97
Sample 21369, NS = 5, 11/16/82 98
Sample 21370, NS = 5, 11/16/82 99
Sample 27745-1, NS = 5, 11/19/82 100
Sample 27745-1, NS = 5, 11/19/82 101
Sample 27745-1, NS = 10, 12/01/82 102
Sample 27746-1, NS = 5, 11/19/82 103
Sample 27746-1, NS = 10, 12/02/82 104
Sample 27747-SS-1, NS = 10, 12/01/82 105
Sample 27747-SS-2, NS = 5, 11/19/82 106
Sample 27748-SS-1, NS = 5, 12/02/82 107
Sample 27748-SS-2, NS = 10, 11/22/82 108
Sample 29173-1, NS = 10, 03/02/83 109
Sample 29173-2, NS = 10, 03/02/83 110
Sample 29173-3, NS = 10, 03/02/83 111
Sample 29174-1, NS = 10, 03/02/83 112
Sample 29174-2, NS = 10, 03/02/83 113
Sample 29174-3, NS = 10, 02/03/83 114

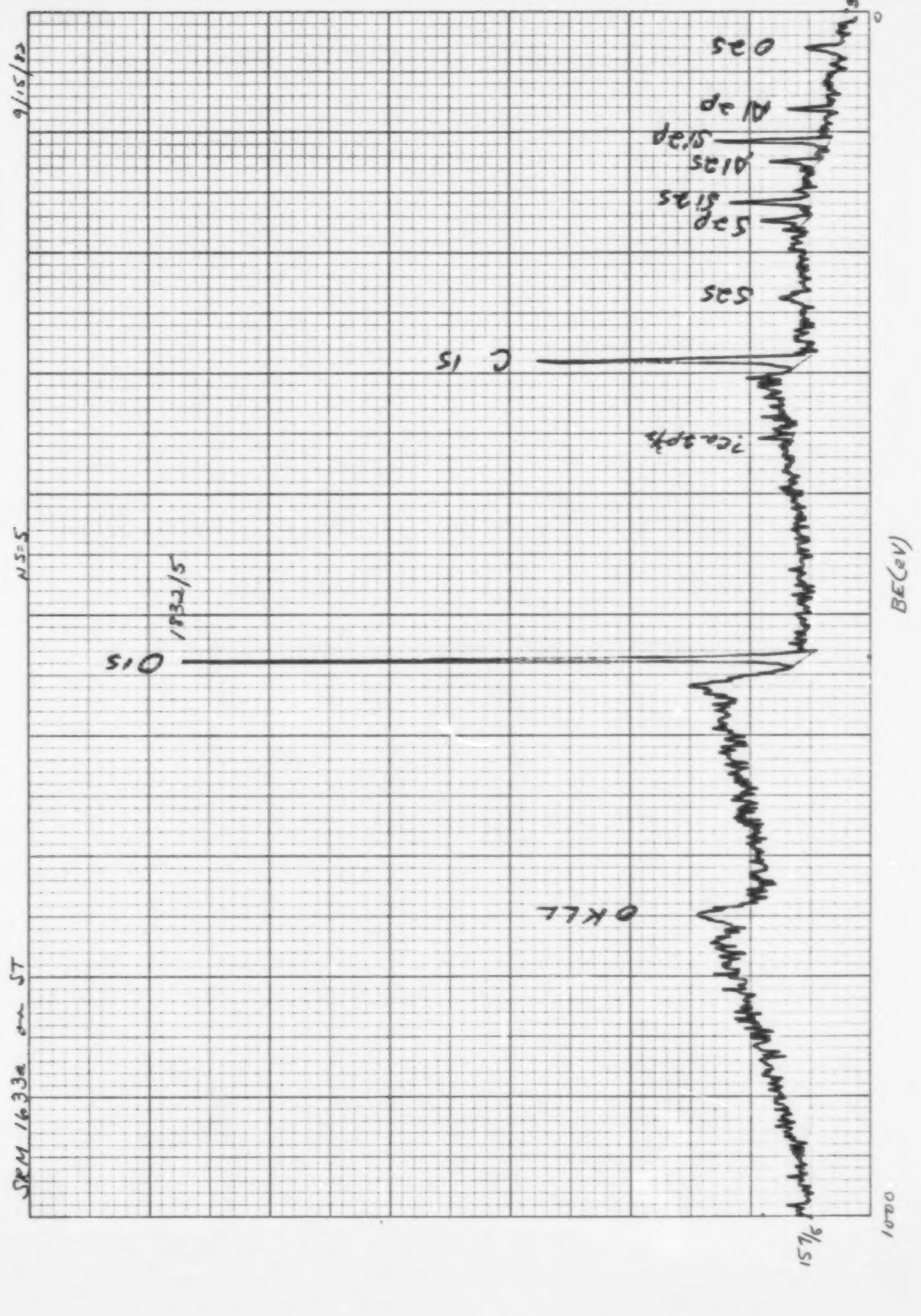
ESCA AFTER LEACHING

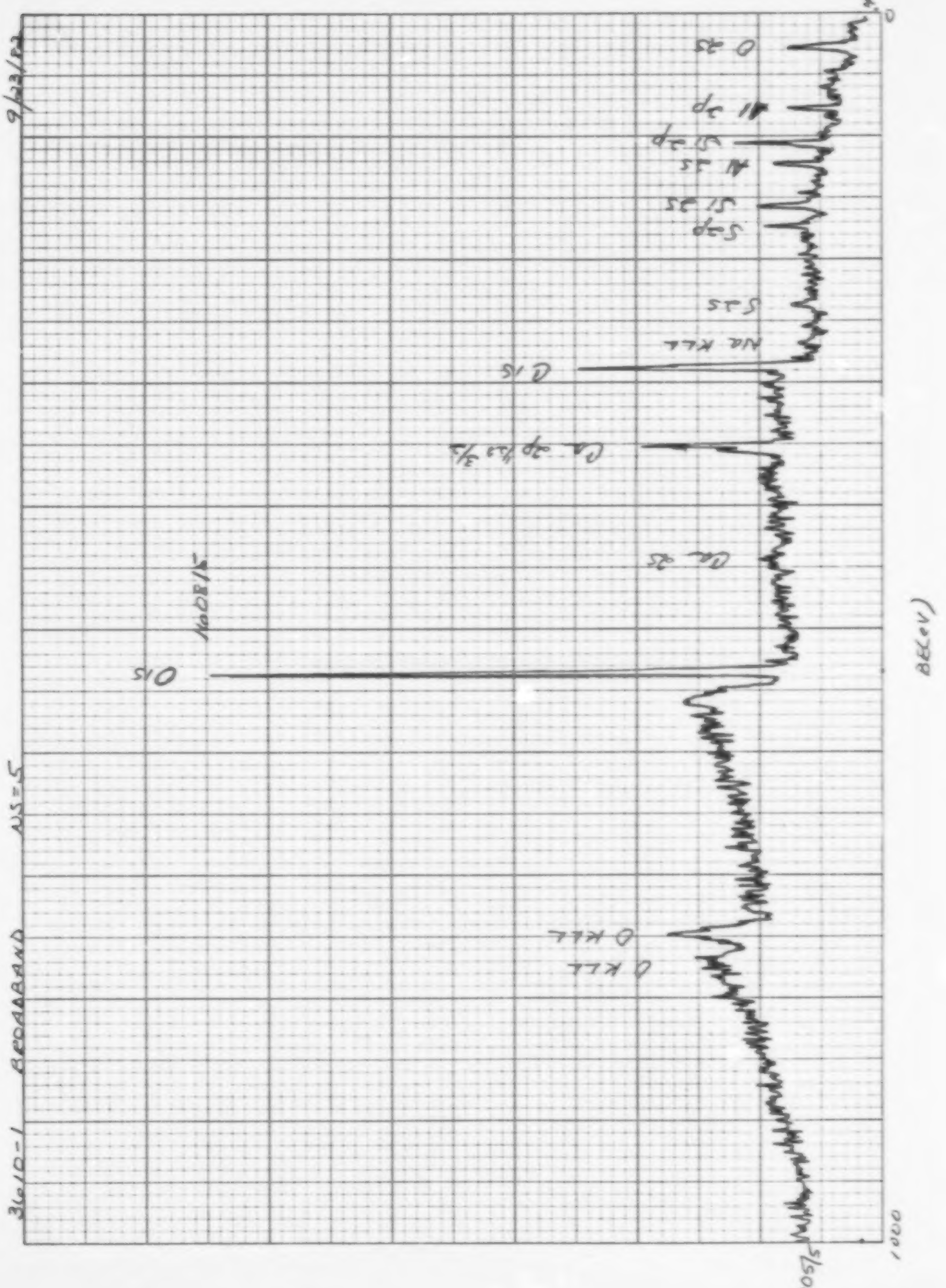
Sample 3610-1-AL-1, NS = 10, 05/10/83 115
Sample 3610-1-AL-2, NS = 10, 05/10/83 116
Sample 9949-1-AL-2, NS = 10, 05/10/83 117
Sample 24616-1-AL-1, NS = 10, 05/10/83 118
Sample 24616-1-AL-2, NS = 10, 05/10/83 119
Sample 27745-L1, NS = 10, 03/14/83 (C.1) 120
Sample 27745-L1, NS = 10, 03/14/83 (C.2) 121
Sample 27745-L2, NS = 10, 03/15/83 (C.1) 122
Sample 27745-L2, NS = 10, 03/15/83 (C.2) 123
Sample 27746-L1, NS = 10, 03/14/83 124
Sample 27746-L2, NS = 10, 03/15/83 125
Sample 29174-L1, NS = 10, 03/14/83 126
Sample 29174-L2, NS = 10, 03/14/83 127

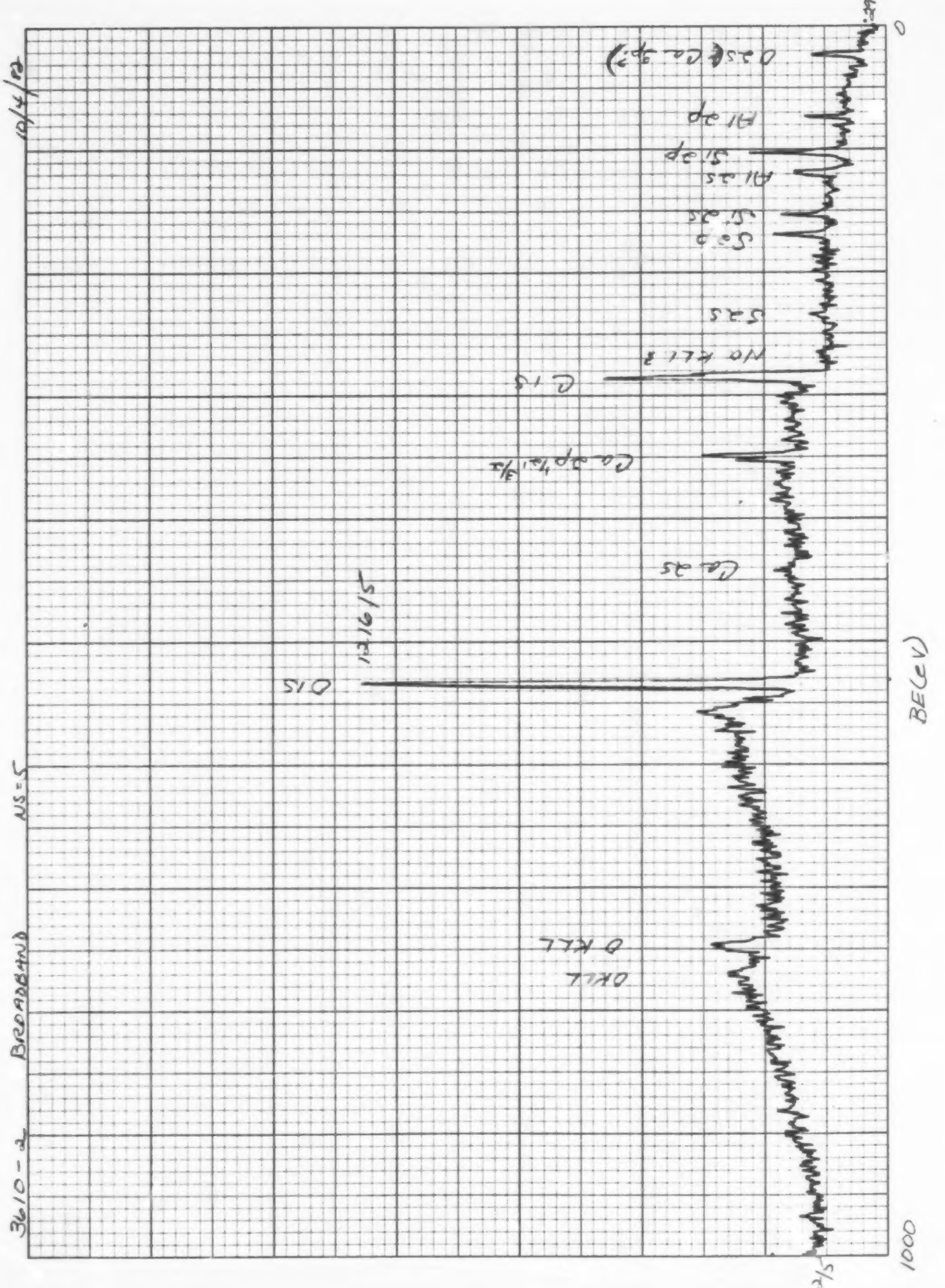

GCA 3610 on SS
NS=5
9/15/82
OKLL
O1S
1224/5
Ca 2S
Ca 2p½,3/2
C 1S
S2S
S 2p
Si 2S
Al 2S
Si 2p
Al 2p
O 2S
1000
BE(eV)
0
159/5
5/65

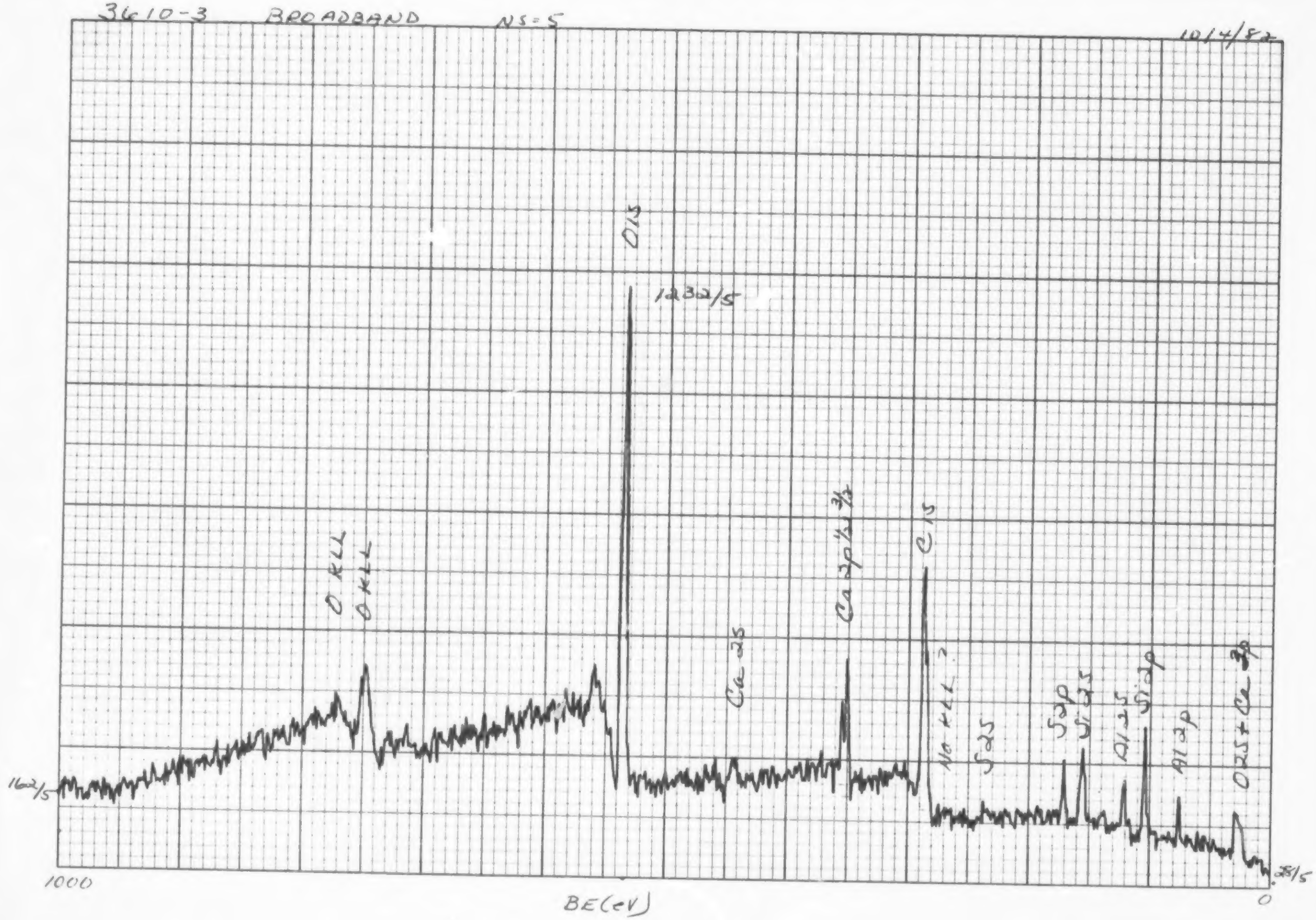

QCA 3610 on ST
NS=5
9/15/80
O 1s
1233/5
O KLL
Ca 2s
Ca 2p½, 3/2
C 1s
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
O 2s
143/5
36/5
1000
BE(eV)
0

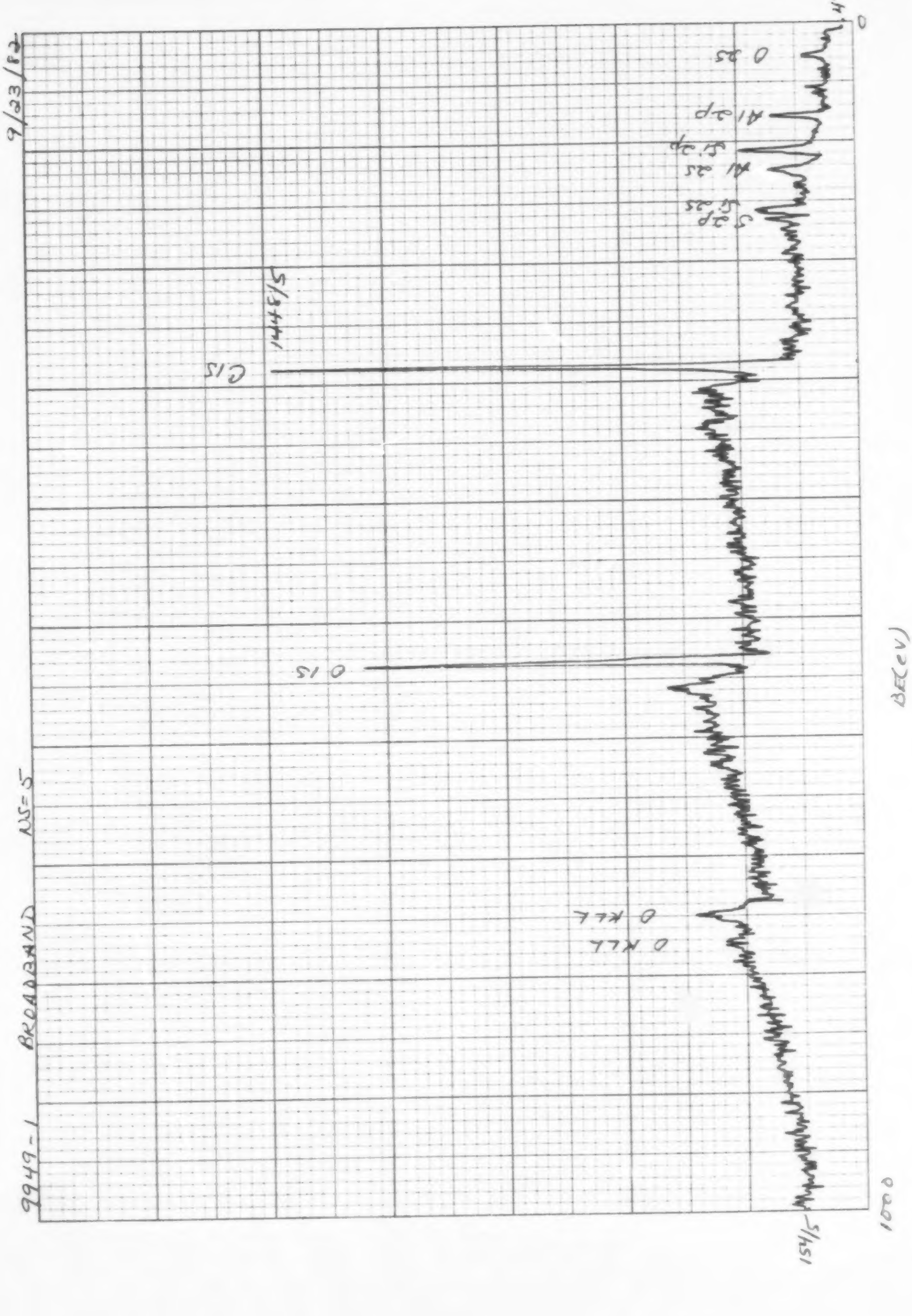

0
1000
BE(eV)
24/5
193/5
O 2s
unknown
Al 2p
Al 2s
Si 2p
S 2p
Si 2s
C 1s
? Ca 2p 3/2
843/5
O 1s
SS Substrate
Breakthrough
8 SCM 16332 on SS
NS=5
9/15/82

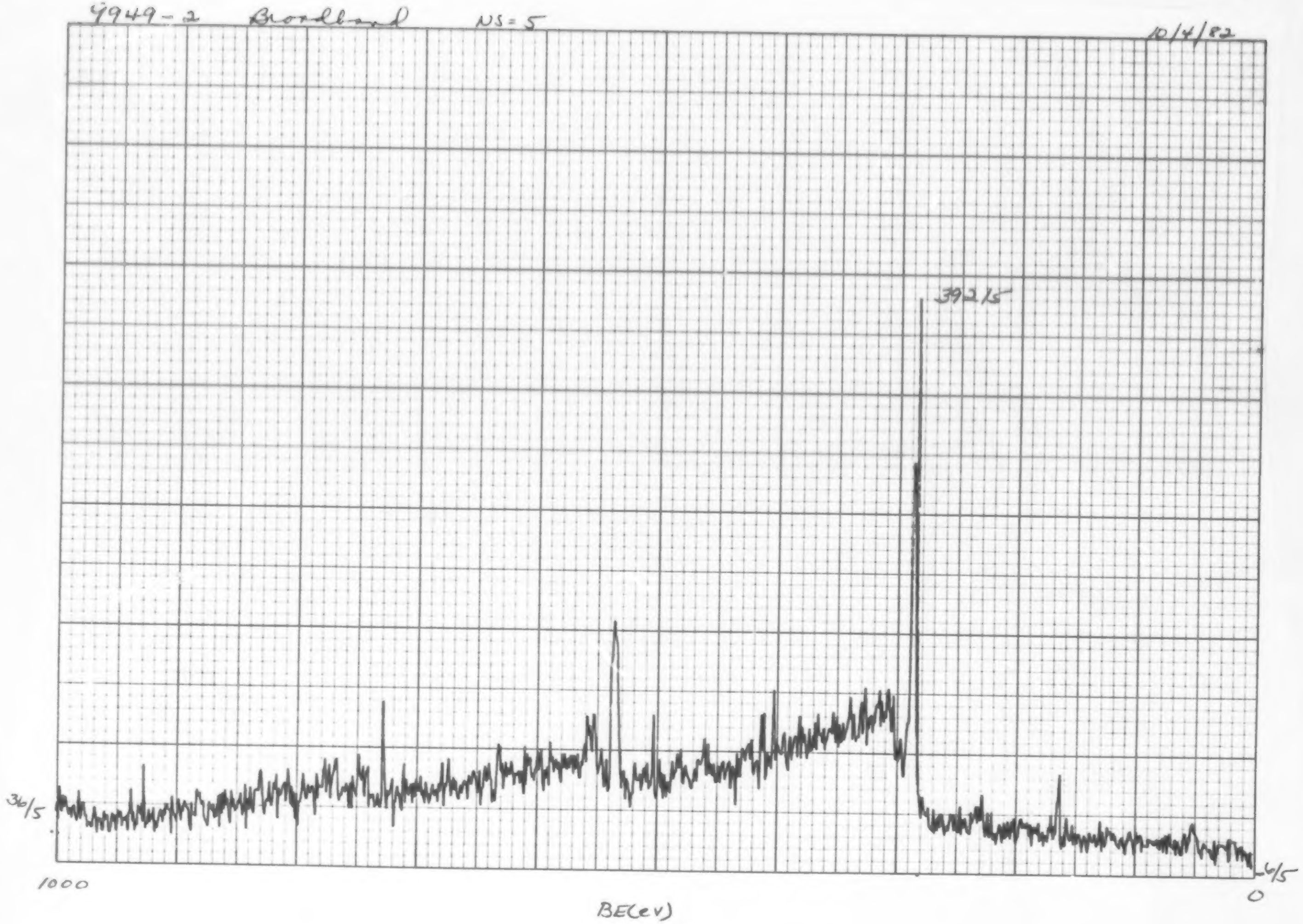
SRM 1633a on ST
NS:5
9/15/82
O 2s
Al 2p
Si 2p
Al 2s
Si 2s
S 2p
S 2s
C 1s
?Ca 2p½
O 1s
1832/5
O KLL
BE(eV)
0
1000
30/5
157/6

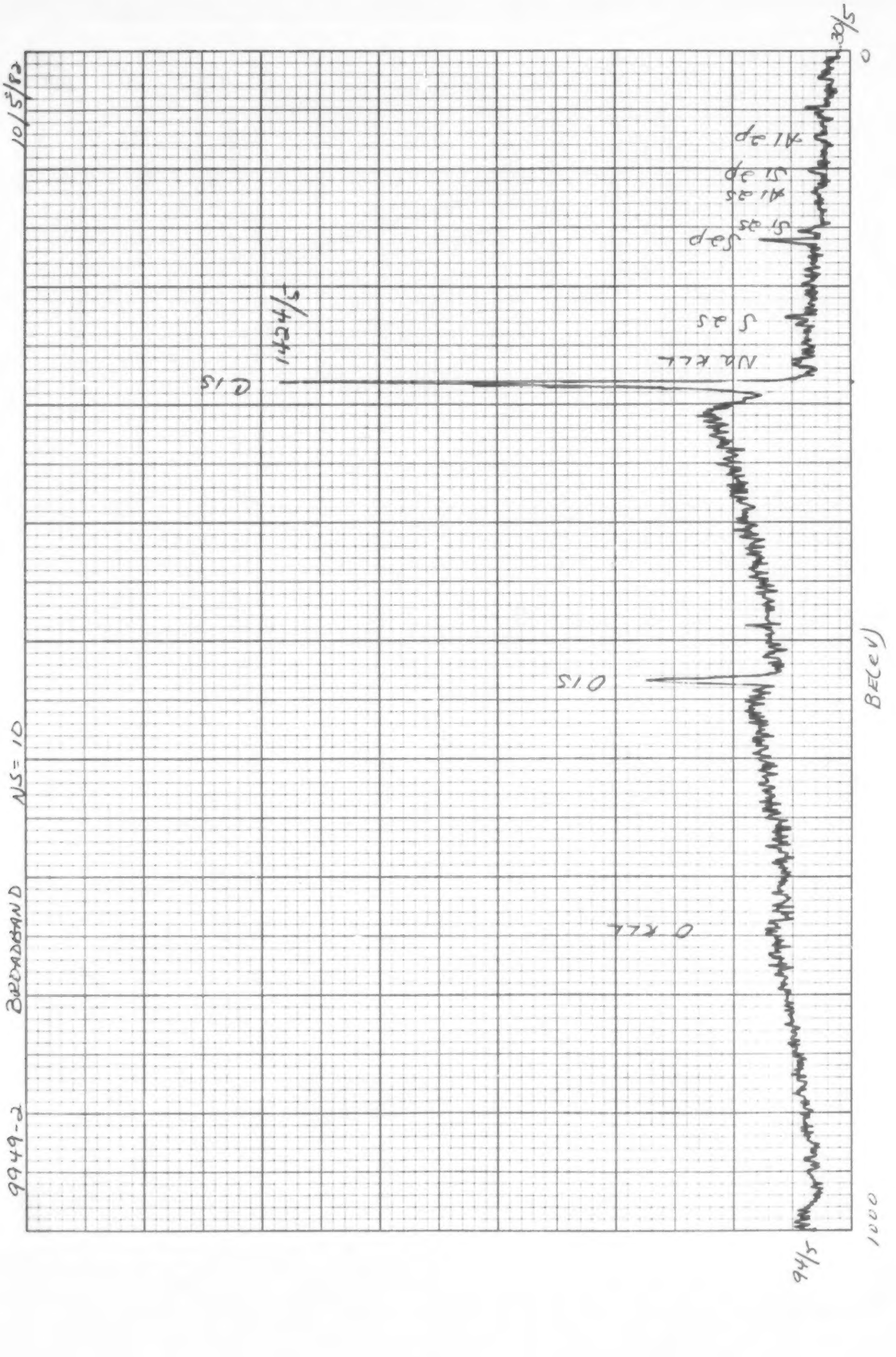

3610-1 BROADBAND
NS=5
9/22/82
0
1000
BE(eV)
463/s
805/s
O 2s
Al 2p
Si 2p
Al 2s
Si 2s
S 2p
S 2s
Na KLL
C 1s
Ca 2p 1/2 3/2
Ca 2s
O 1s
14008/s
O KLL
O KLL

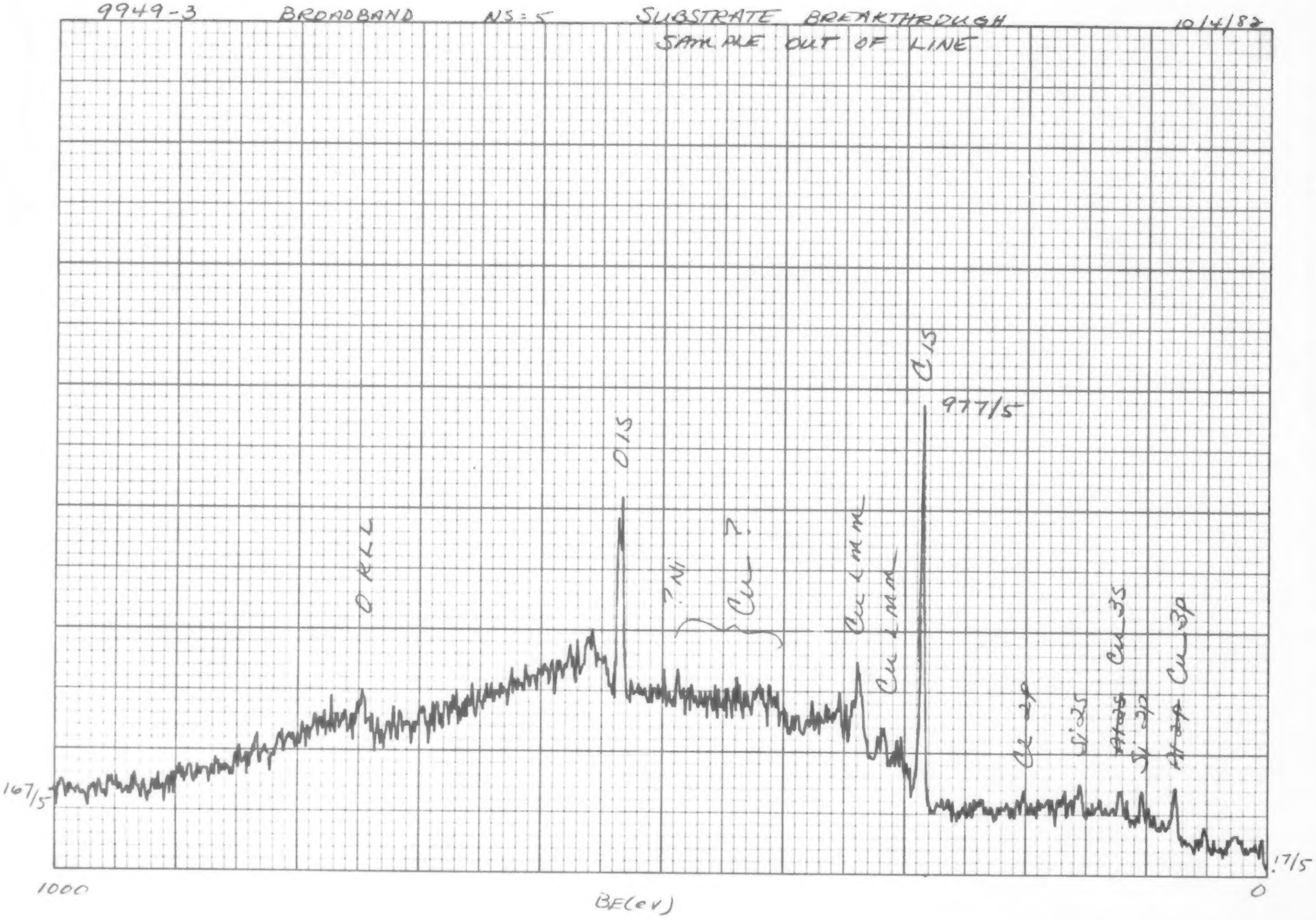

3610-2
BROADBAND
NS=5
10/4/82
BE(eV)
0
1000
29/5
162/5
1216/5
O 2s (Ca 3p?)
Al 2p
Si 2p
Al 2s
Si 2s
S 2p
S 2s
Na KLL ?
C 1s
Ca 2p1/2,3/2
Ca 2s
O1s
O KLL
OKLL

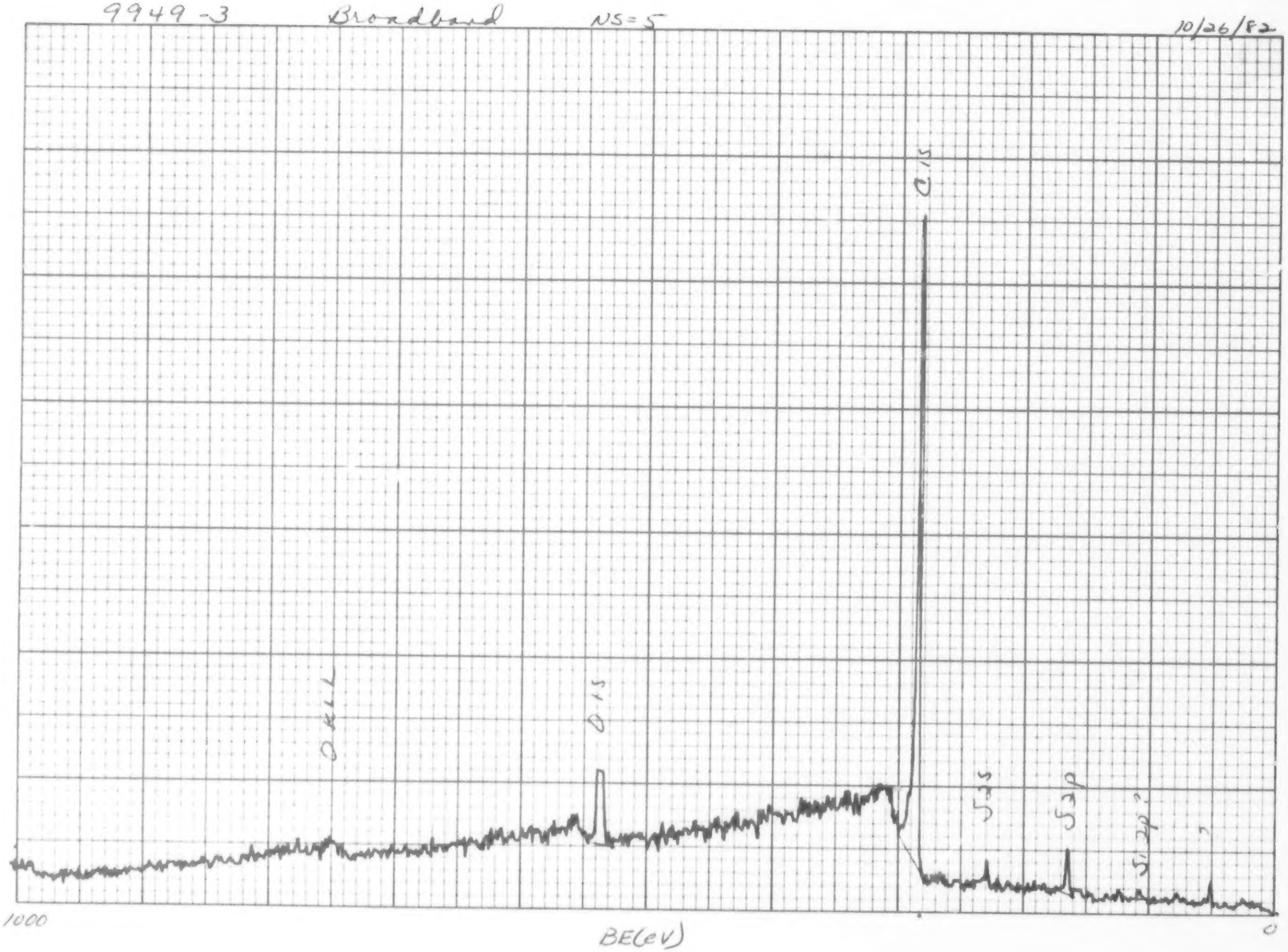

3610-3 BROADBAND NS=5
10/4/82
O KLL
O KLL
O1s
1232/5
Ca 2s
Ca 2p½ 3/2
C 1s
Na KLL ?
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
O2s + Ca 3p
162/5
28/5
1000
BE(eV)
0

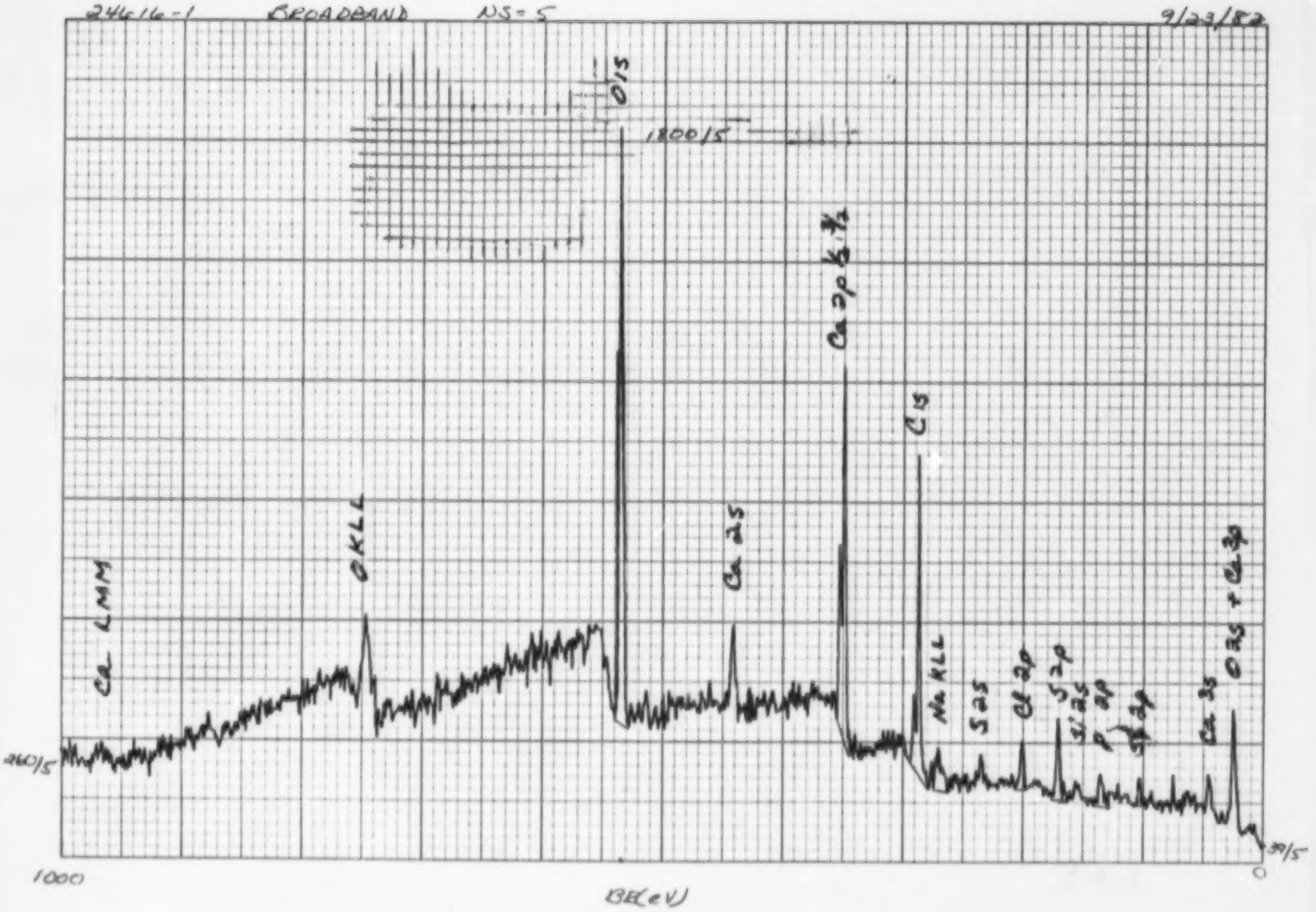

9949-1
BROADBAND
NS=5
9/23/82
C1S
1443/5
O 1S
O KLL
O KLL
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
O 2s
47/5
0
1000
154/5
BE(eV)

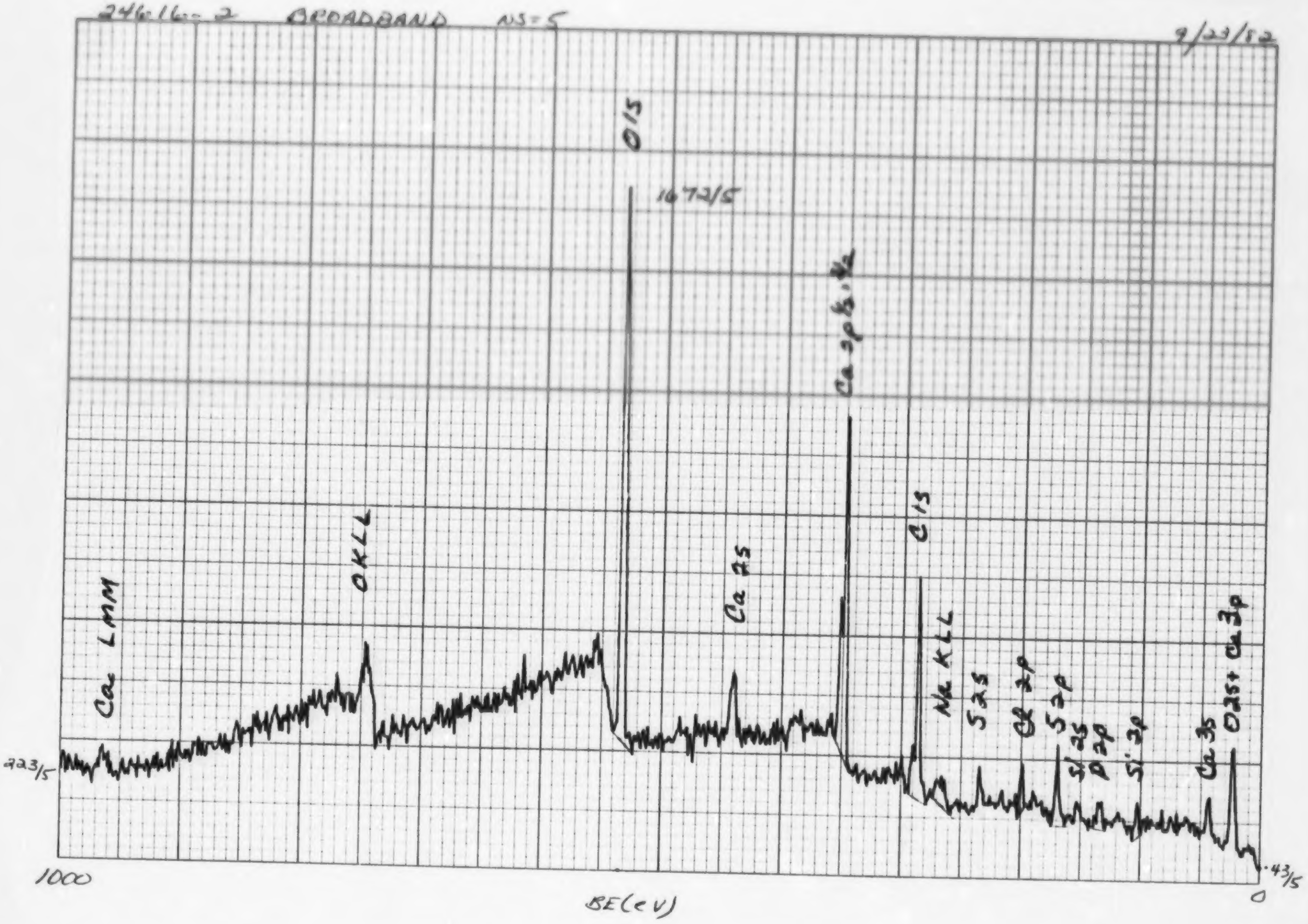

4949-2 Broadband NS=5
10/4/82
392/5
36/5
6/5
1000
0
BE(ev)

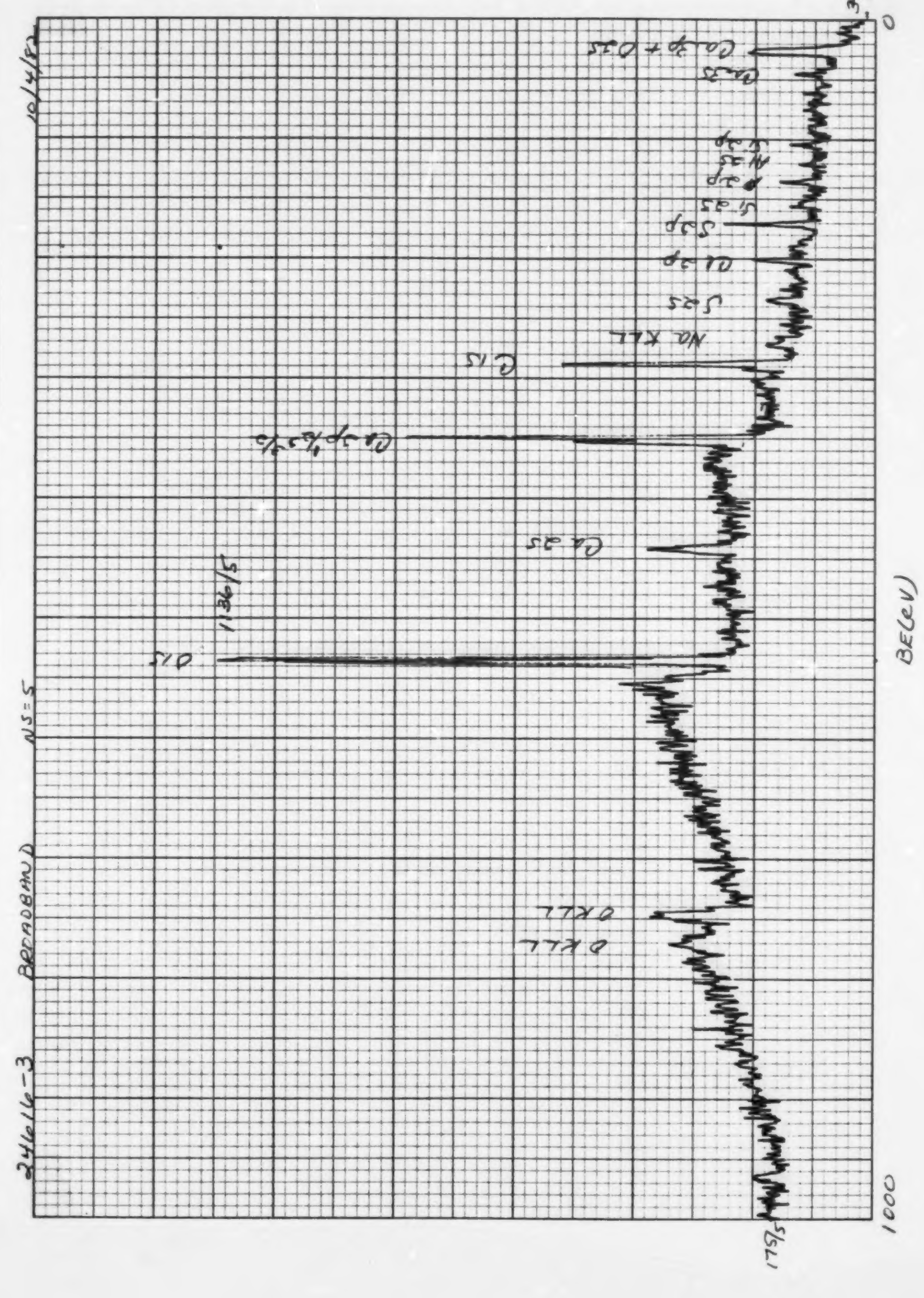

10/5/82
9949-2
BROADBAND
NS=10
1424 c/s
C 1s
O 1s
O KLL
Na KLL
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
30 c/s
94 c/s
0
1000
BE(eV)

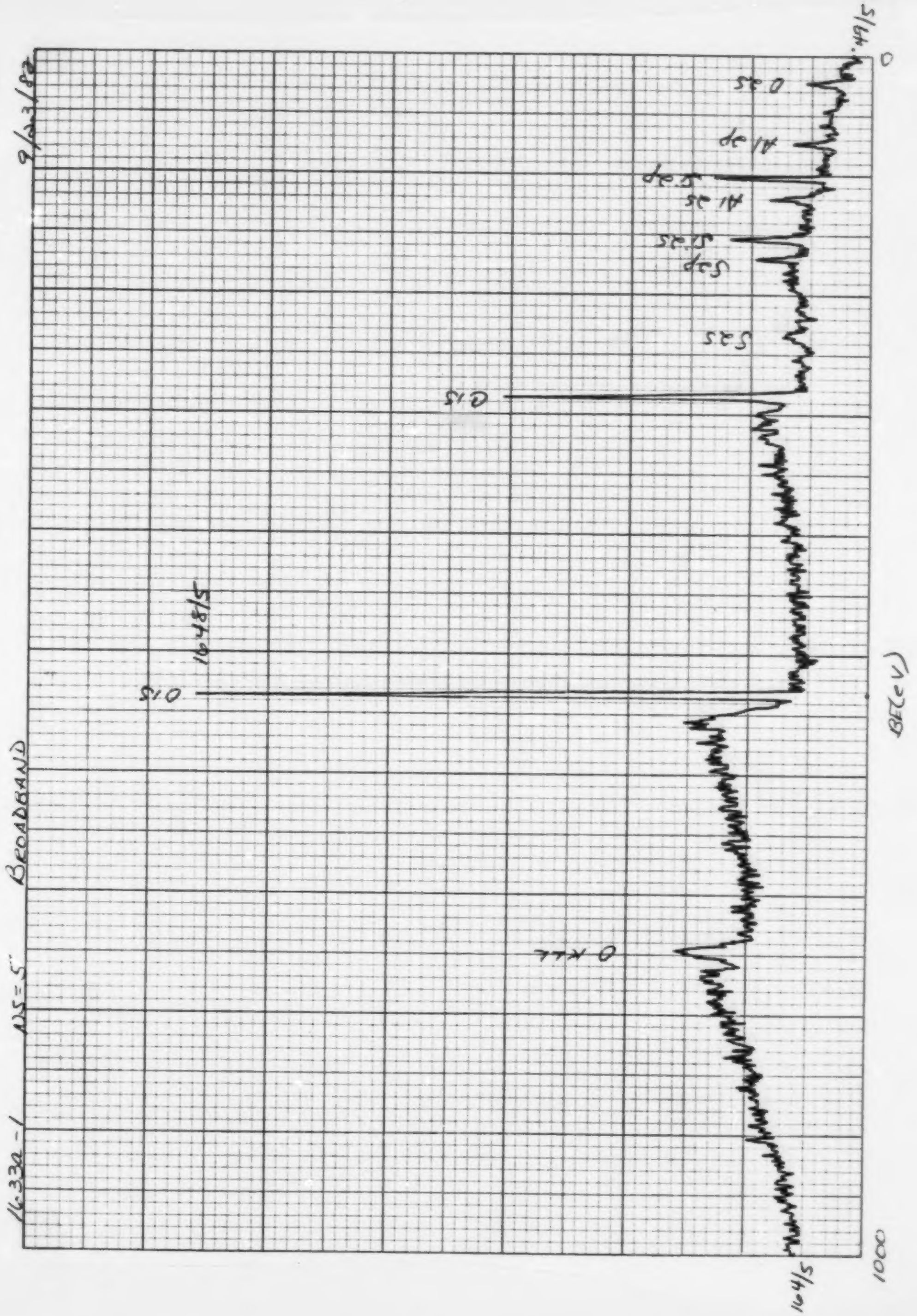

9949-3
BROADBAND
NS=5
SUBSTRATE BREAKTHROUGH
SAMPLE OUT OF LINE
10/4/82
O KLL
O 1S
? Ni
Cu ?
Cu LMM
Cu LMM
C 1S
977/5
Cl 2p
Si 2S
~~Al 2s~~ Cu 3S
Si 2p
~~Al 2p~~ Cu 3p
167/5
17/5
1000
BE(eV)
0

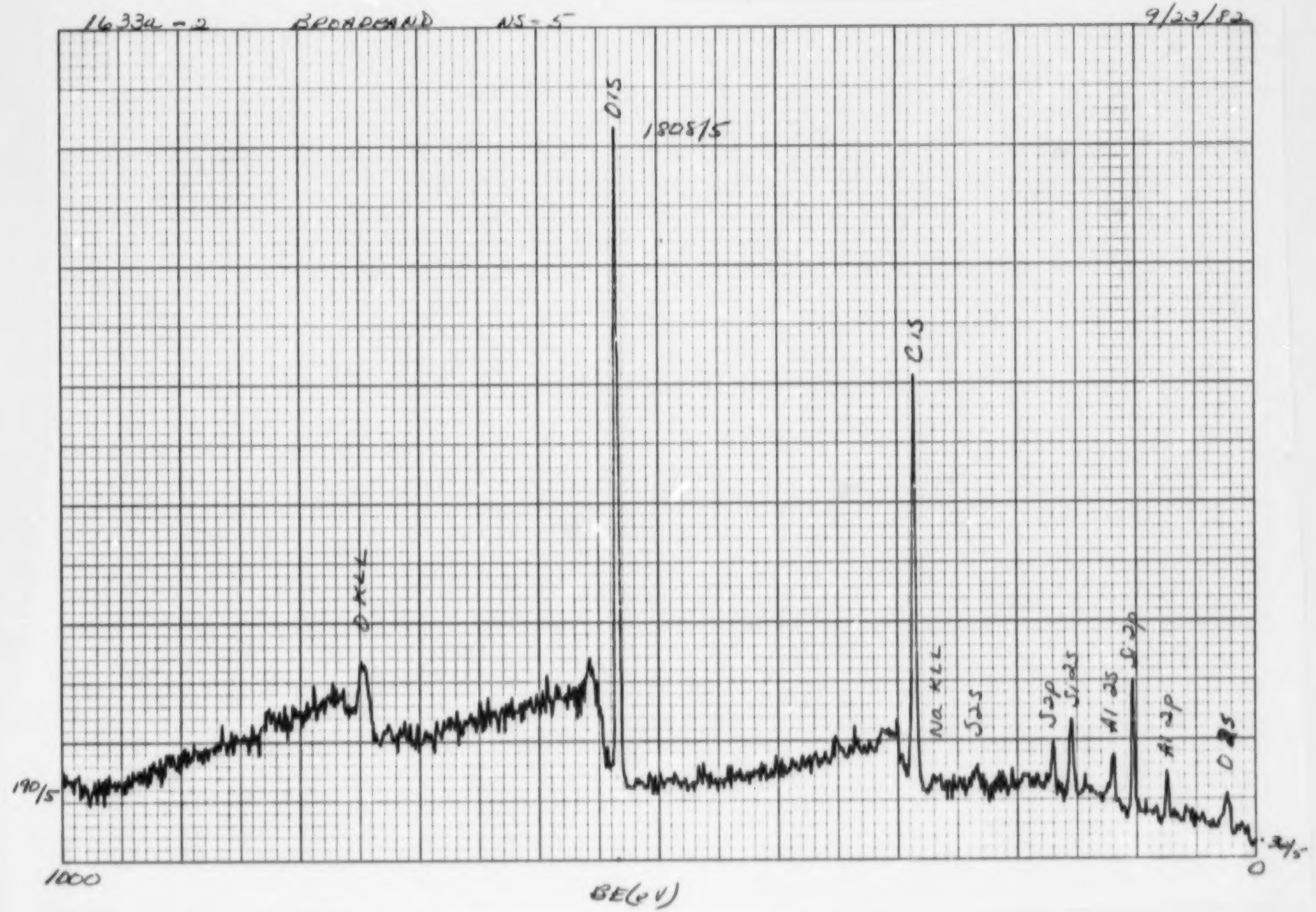

9949-3
Broadband
NS=5
10/26/82
C 1s
O KLL
O 1s
S 2s
S 2p
Si 2p?
1000
BE(eV)
0

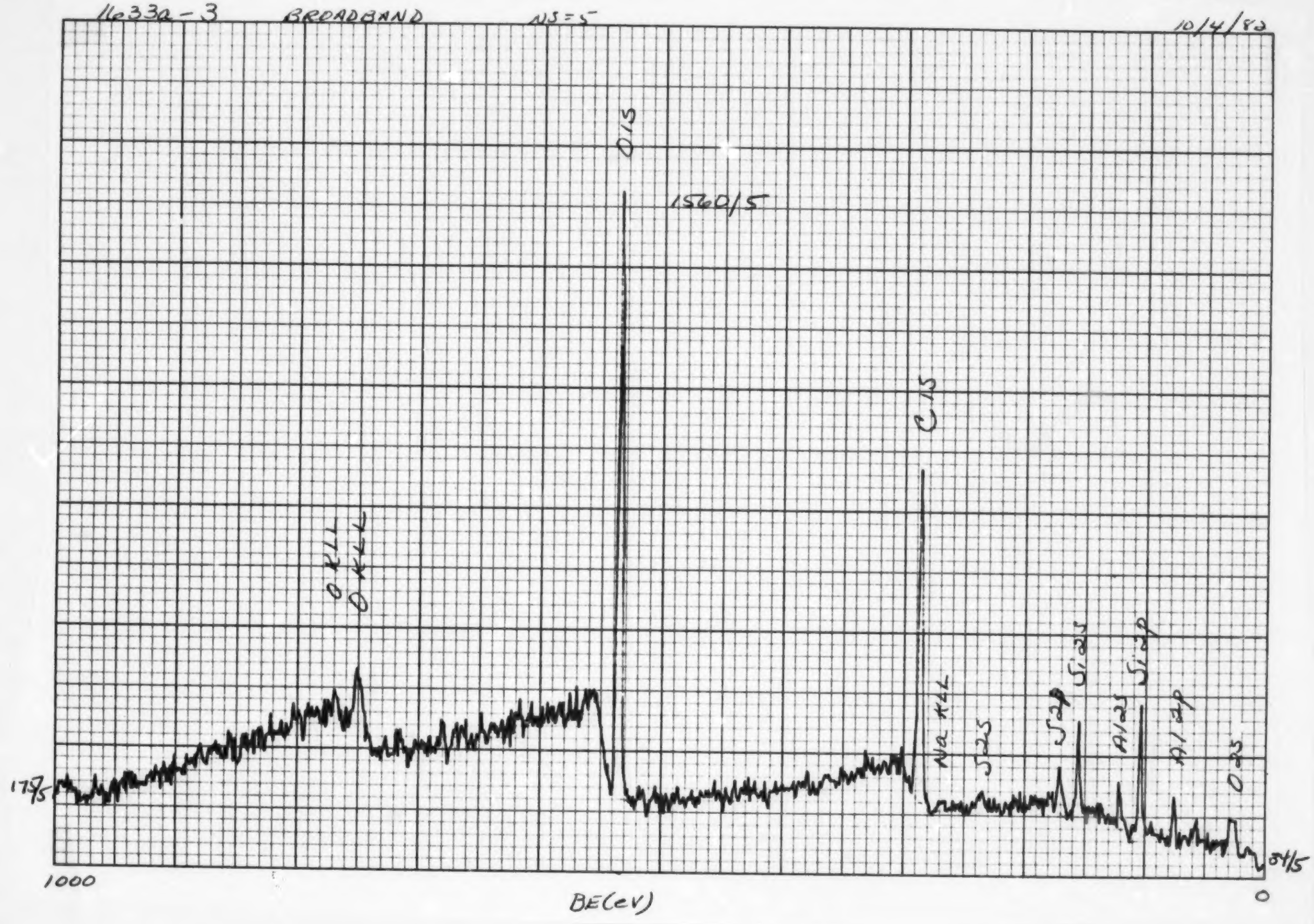

24616-1
BROADBAND
NS=5
9/23/82
O1s
1800/5
Ca 2p ½, 3/2
C1s
Ca 2s
OKLL
Ca LMM
Na KLL
S 2s
Cl 2p
S 2p
Si 2s
P 2p
Si 2p
Ca 3s
O 2s + Ca 3p
260/5
30/5
1000
0
BE(eV)

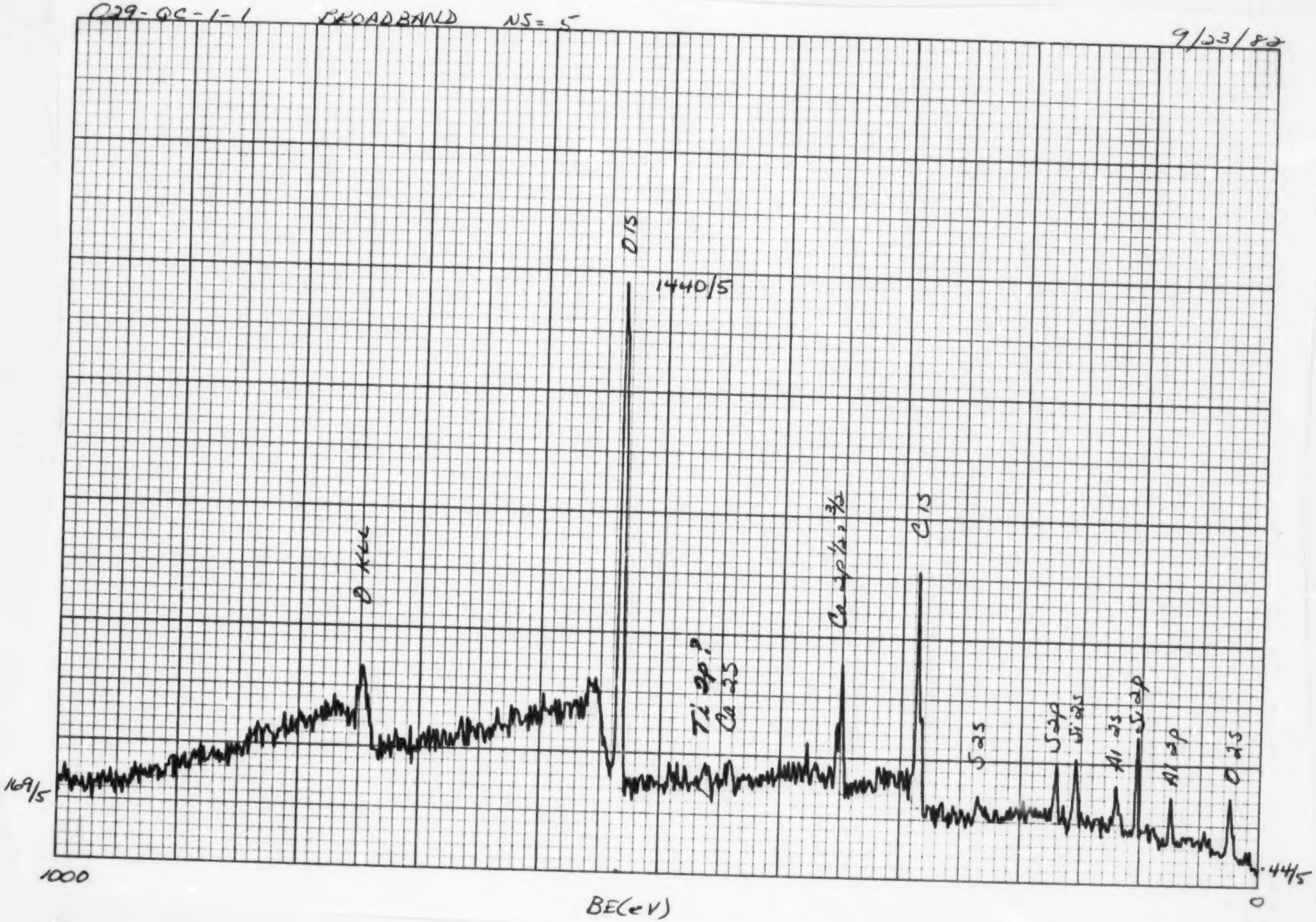

24616-2 BROADBAND NS=5
9/23/82
O1s
1672/5
Ca 2p3/2,1/2
C1s
Ca 2s
OKLL
Ca LMM
Na KLL
S 2s
Cl 2p
S 2p
Si 2s
P 2p
Si 2p
Ca 3s
O2s+ Ca 3p
223/5
.43/5
1000
0
BE(eV)

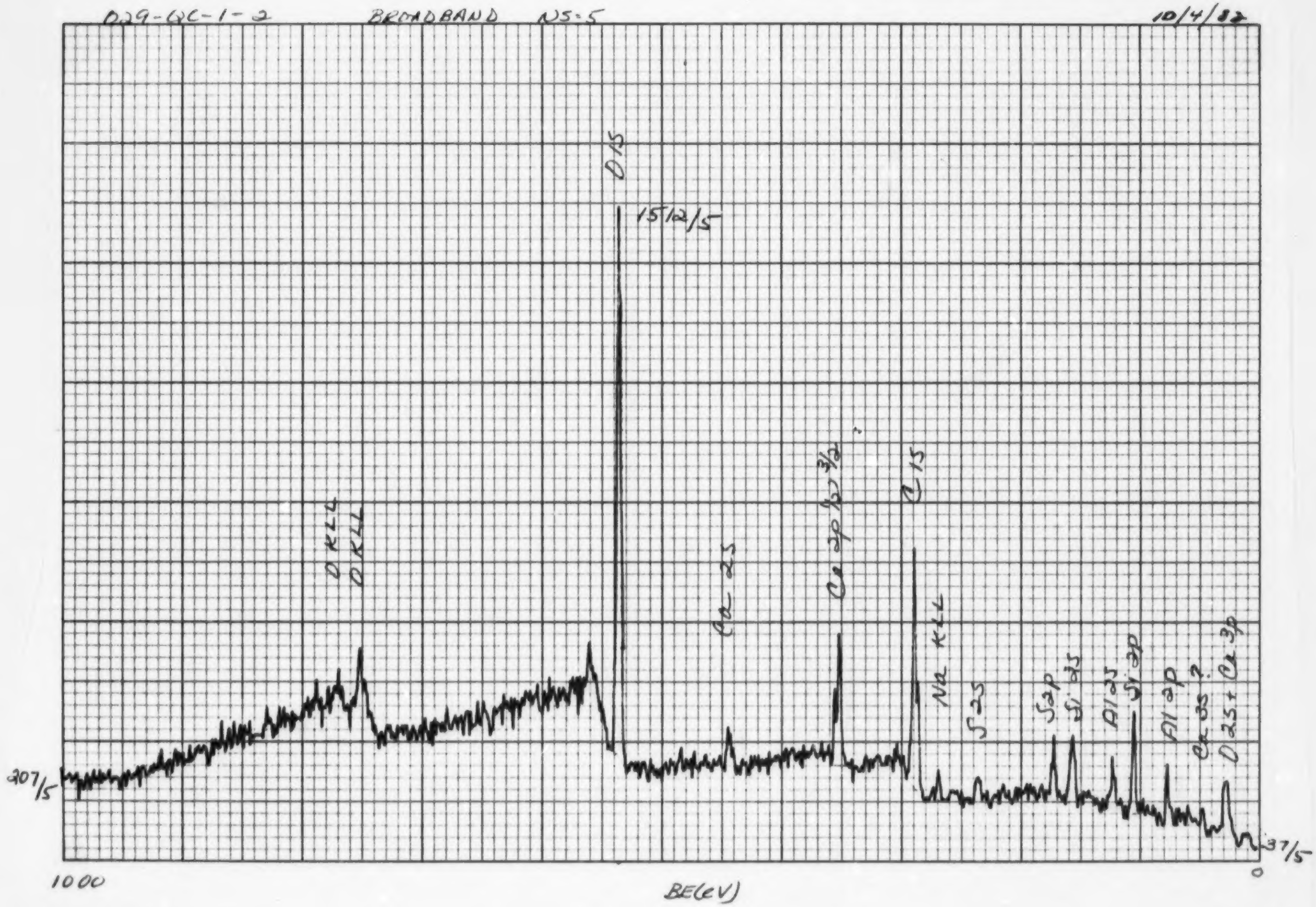

24166-3
BREADBAND
NS=5
10/4/82
O KLL
O KLL
O 1s
1136/5
Ca 2s
Ca 2p 3/2, 1/2
C 1s
Na KLL
S 2s
Cl 2p
S 2p
Si 2s
P 2p
N 2s
Si 2p
Ca 3s
Ca 3p + O 2s
34/5
0
1000
179/5
BE(eV)

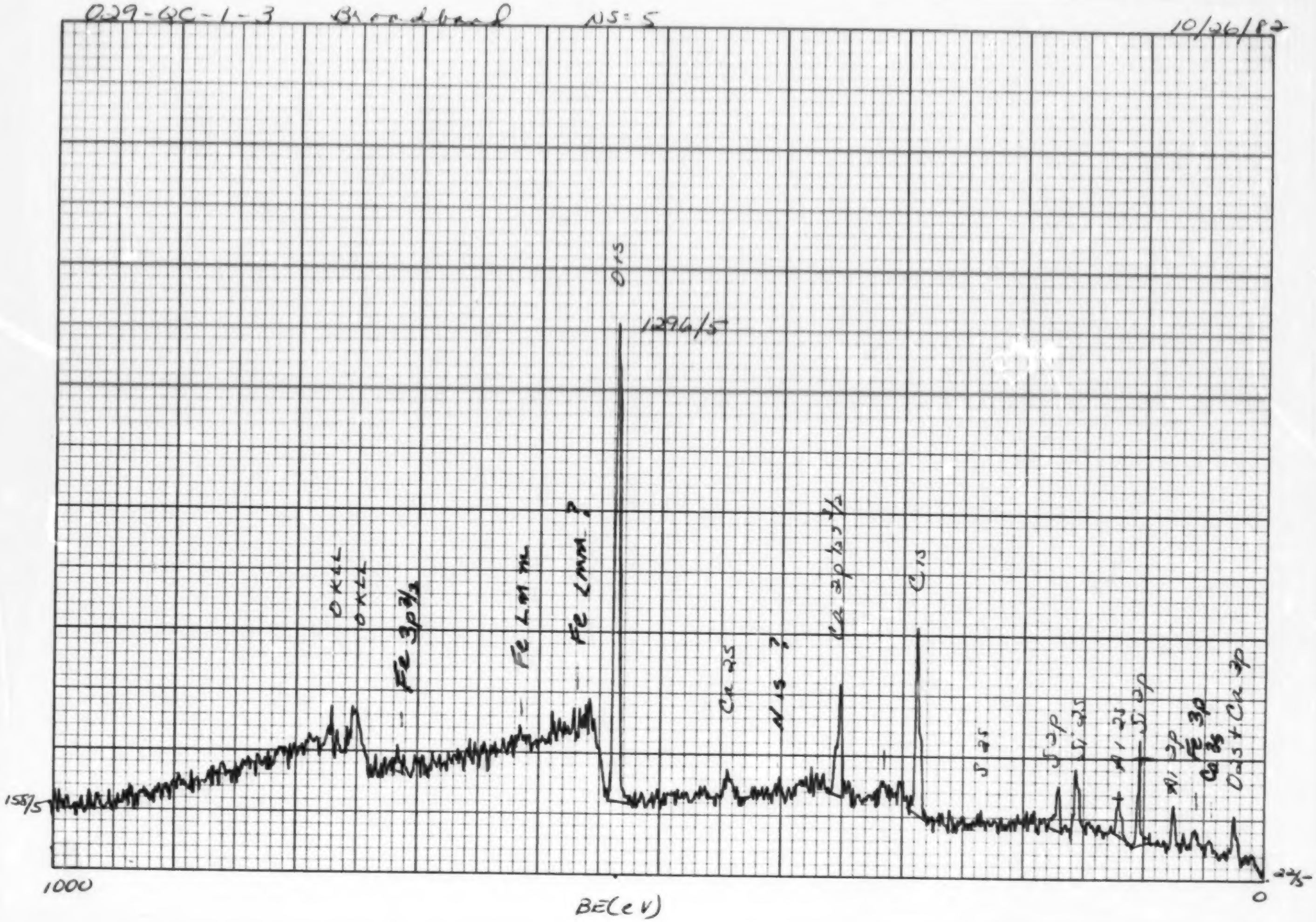

16-33a-1
NS=5
BROADBAND
9/23/82
O 1s
1648/S
O KLL
C 1s
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
O 2s
.49/S
0
104/S
1000
BE(eV)

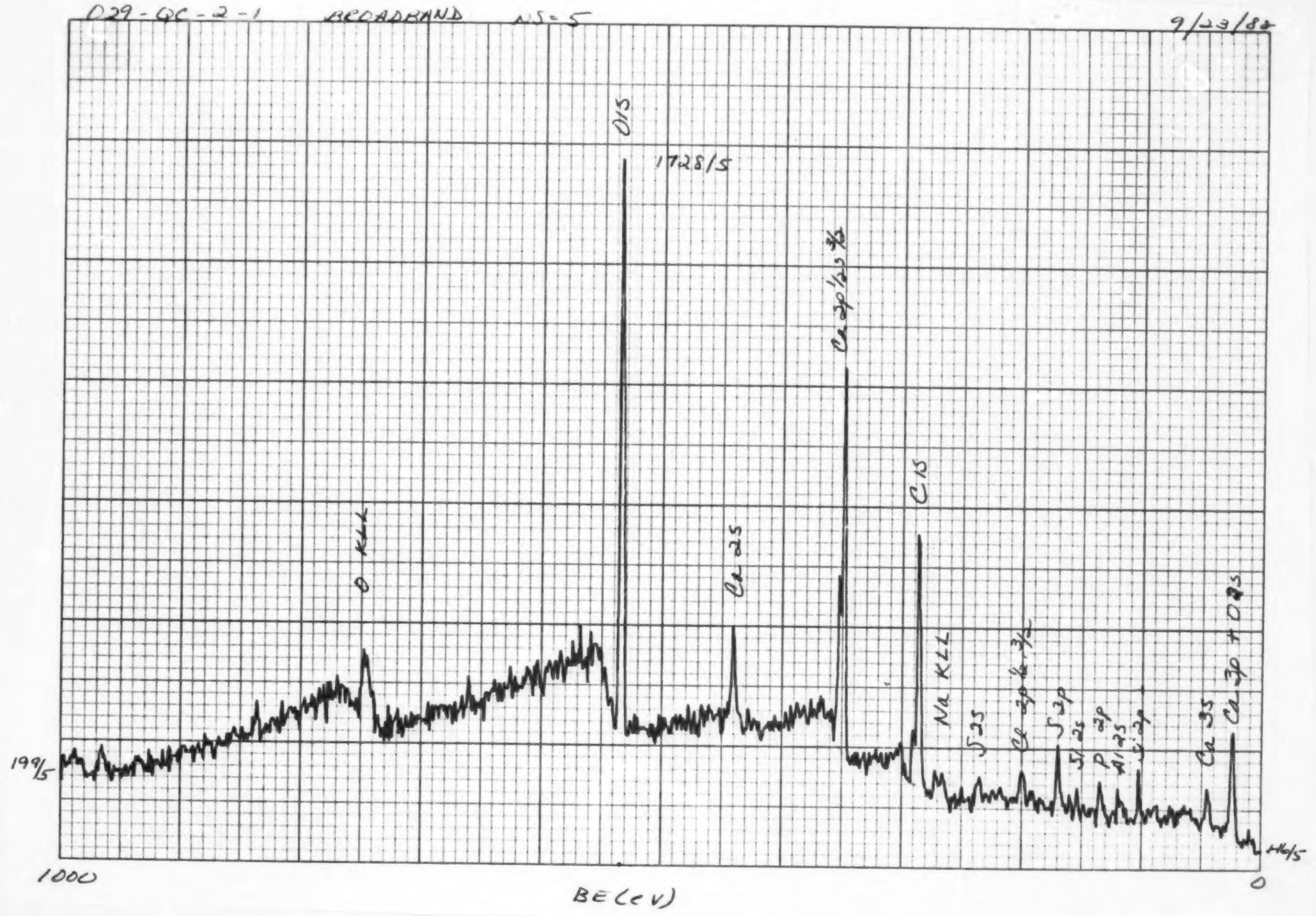

1633a - 2
BROADBAND
NS = 5
9/23/82
O1S
1808/S
C1S
O KLL
Na KLL
S2S
S2p
Si2s
Al 2s
Si2p
Al 2p
O 2s
190/S
34/S
1000
0
BE(eV)

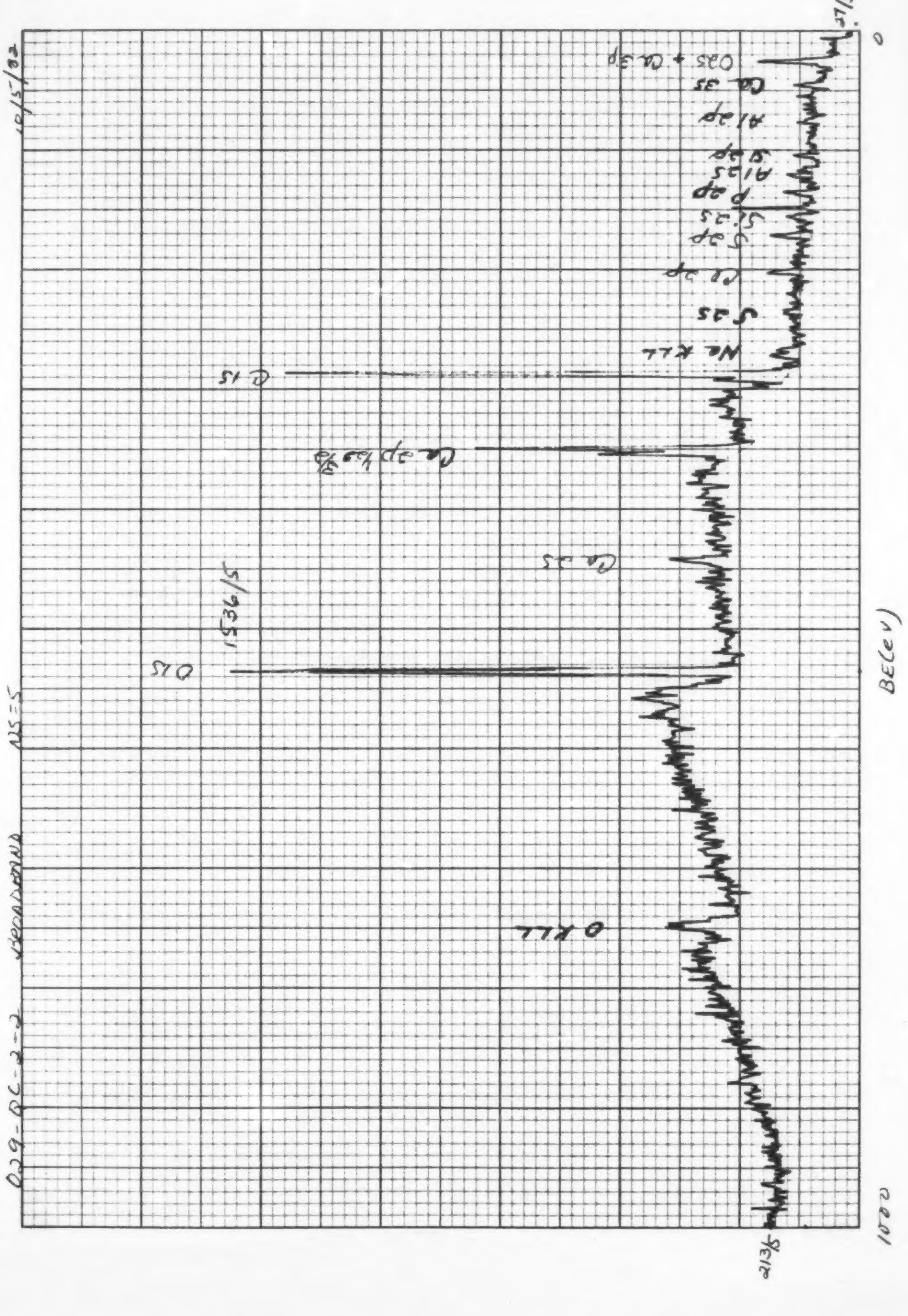

1633a - 3
BROADBAND
NS=5
10/4/82
O 1s
1560/5
C 1s
O KLL
O KLL
Na KLL
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
O 2s
177/5
84/5
1000
0
BE(eV)

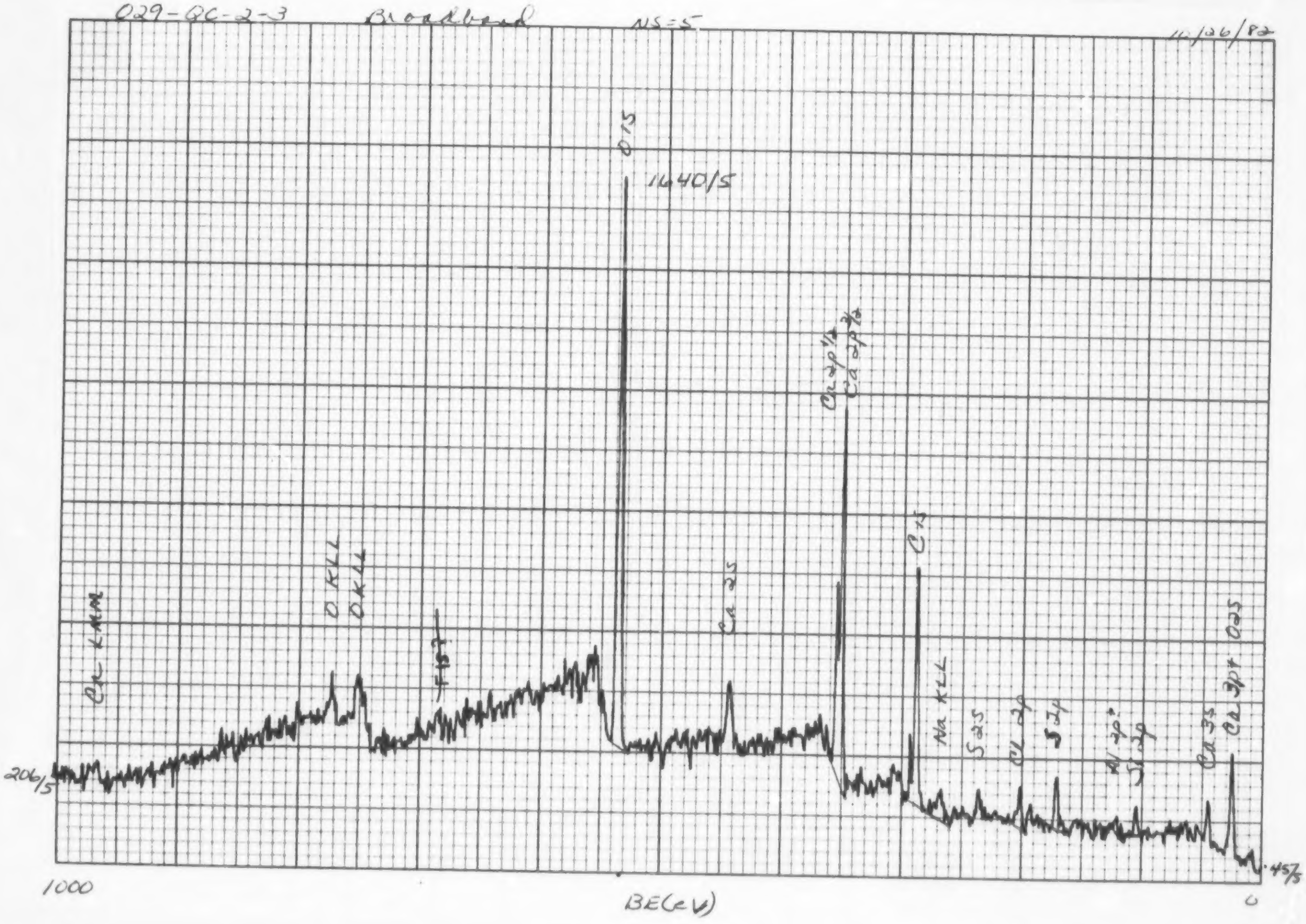

O29-QC-1-1
BROADBAND
NS= 5
9/23/82
O KLL
O 1s
1440/5
Ti 2p?
Ca 2s
Ca 2p1/2, 3/2
C 1s
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
O 2s
169/5
.44/5
1000
BE(eV)
0

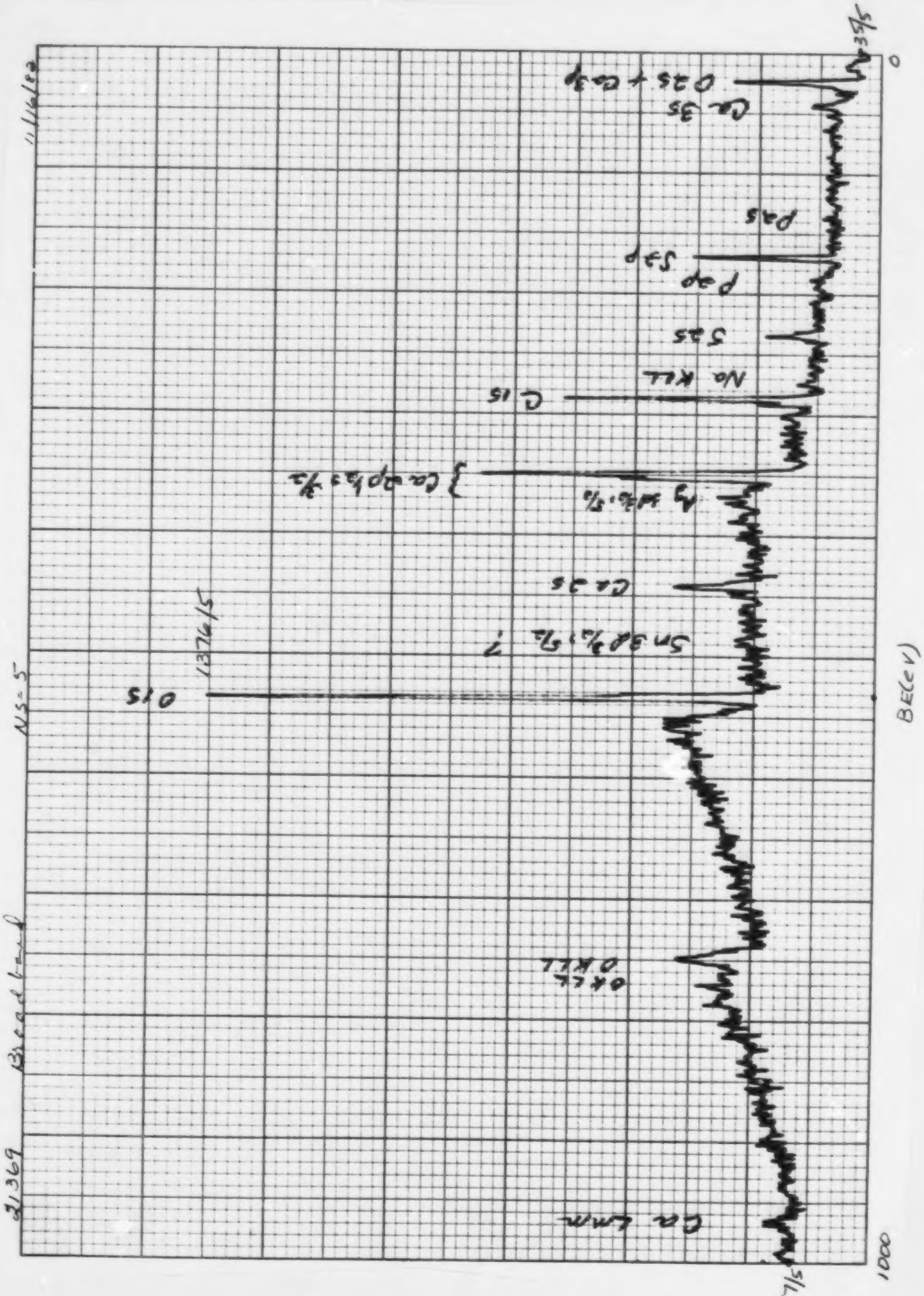

D29-QC-1-2
BROADBAND NS=5
10/4/82
O KLL
O KLL
O 1s
1512/5
Ca 2s
Ca 2p 1/2 3/2
C 1s
Na KLL
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
Ca 3s ?
O 2s + Ca 3p
207/5
37/5
1000
BE(eV)
0

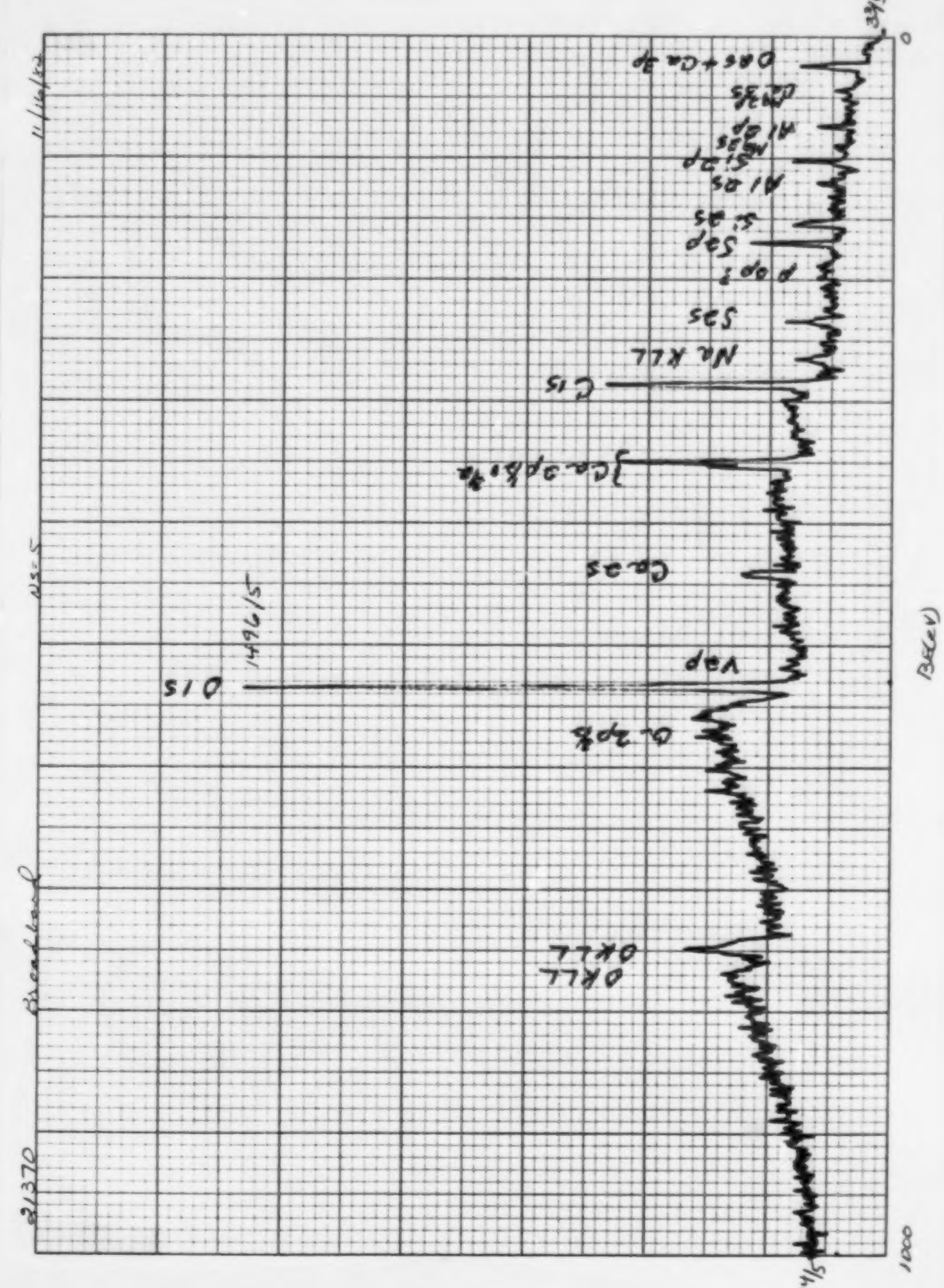

029-QC-1-3 Broadband NS=5
10/26/82
O 1s
1294/5
OKLL
OKLL
Fe 3p3/2
Fe LMM
Fe LMM ?
Cr 2s
N 1s ?
Cr 2p1/2 3/2
C 1s
S 2s
S 2p
Si 2s
Al 2s
Si 2p
Al 2p
Fe 3p
Ca 3s
O 2s + Cr 3p
158/5
-2 2/5-
1000
BE(eV)
0

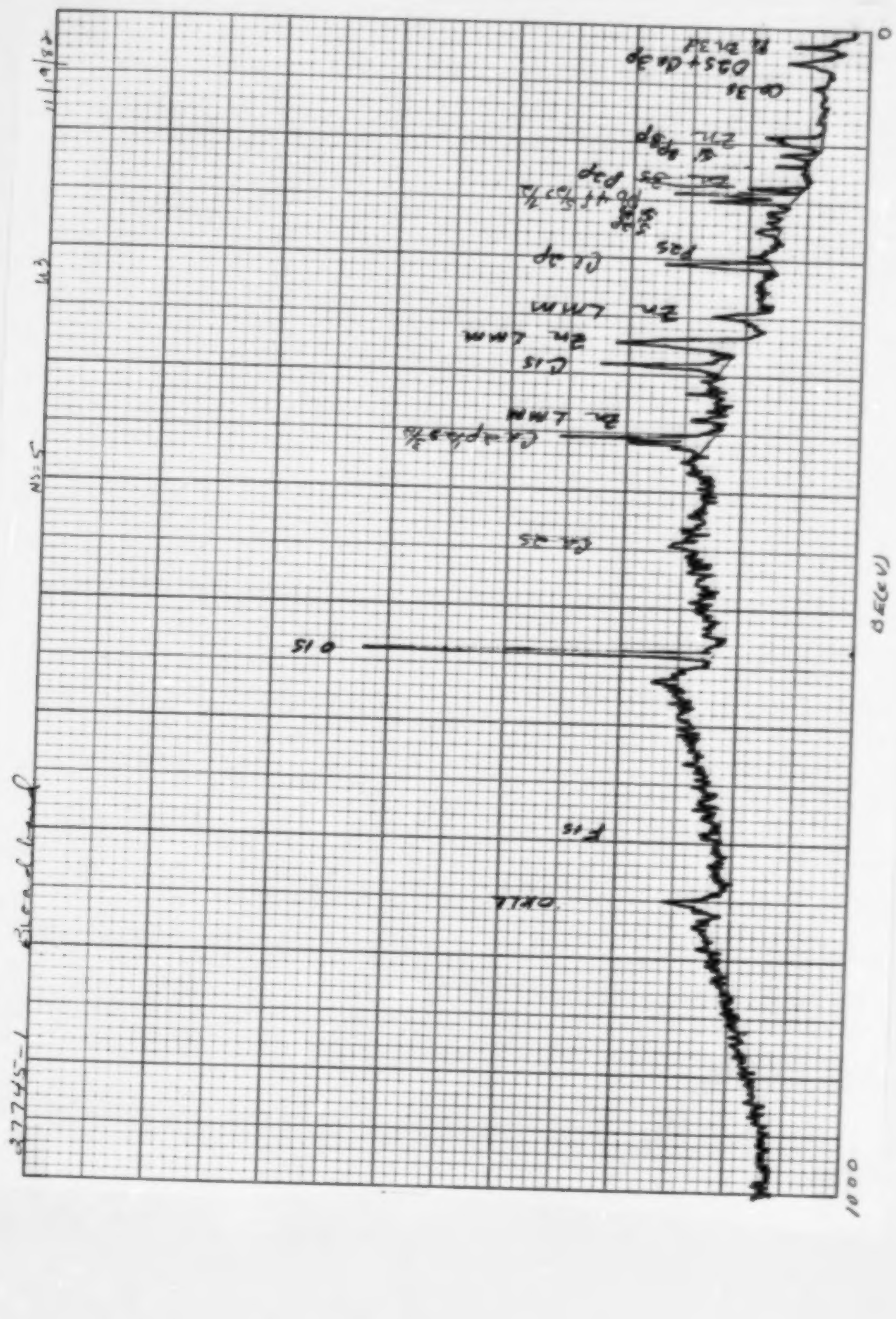

D29-QC-2-1
BROADBAND
NS=5
9/23/88
O1S
1728/S
Ca 2p1/2 3/2
C1S
O KLL
Ca 2S
Na KLL
S 2S
Cl 2p1/2 3/2
S 3p
Si 2S
P 2p
Al 2S
Si 2p
Ca 3S
Ca 3p + O 2S
199/S
1000
BE (eV)
0

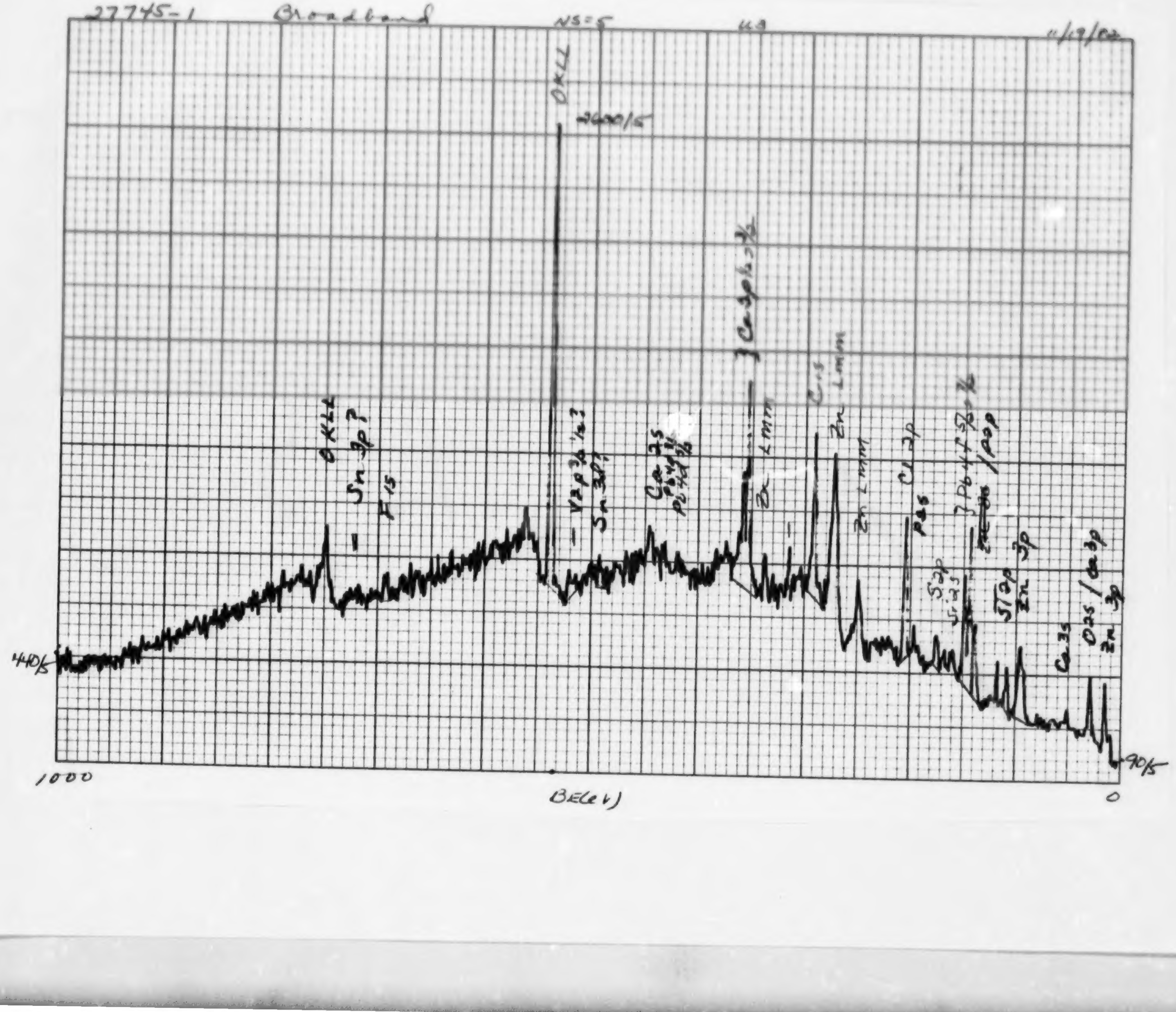

D29-DC-2-2
BROADBAND
NS=5
10/15/82
BE(eV)
0
1000
27/5
213/5
O2s + Ca 3p
Ca 3s
Al 2p
Si 2p
Al 2s
P 2p
Si 2s
S 2p
Cl 2p
S 2s
Na KLL
C 1s
Ca 2p1/2 3/2
Ca 2s
O1s
1536/5
O KLL

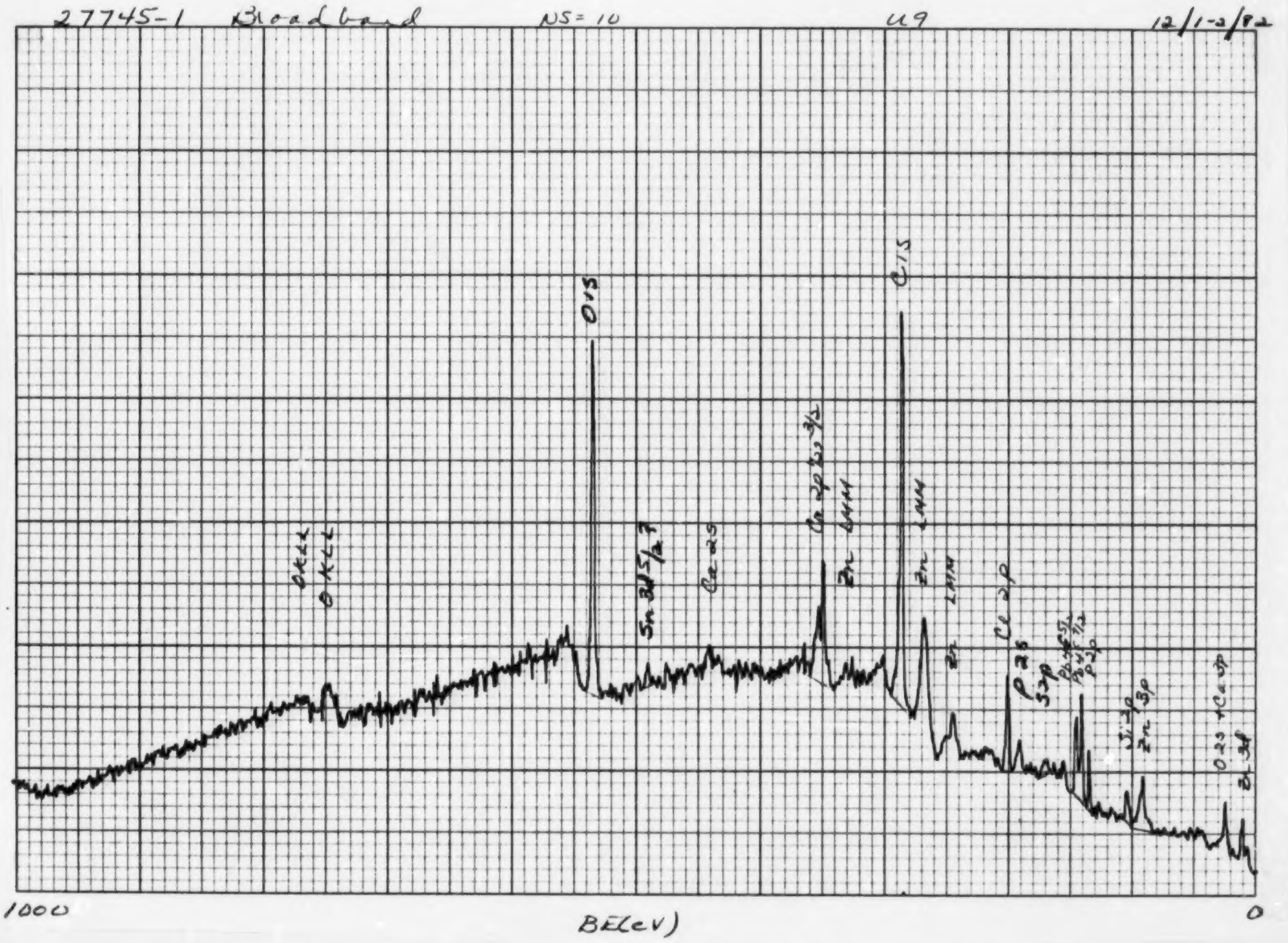

029-QC-2-3
Broadband
NS=5
11/26/82
O 1s
1640/5
Ca 2p½
Ca 2p3/2
C 1s
Ca 2s
Ca KMM
O KLL
O KLL
F 1s?
Na KLL
S 2s
Cl 2p
S 2p
Al 2p?
Si 2p
Ca 3s
Ca 3p
O 2s
206/5
.45/5
1000
BE(eV)
0

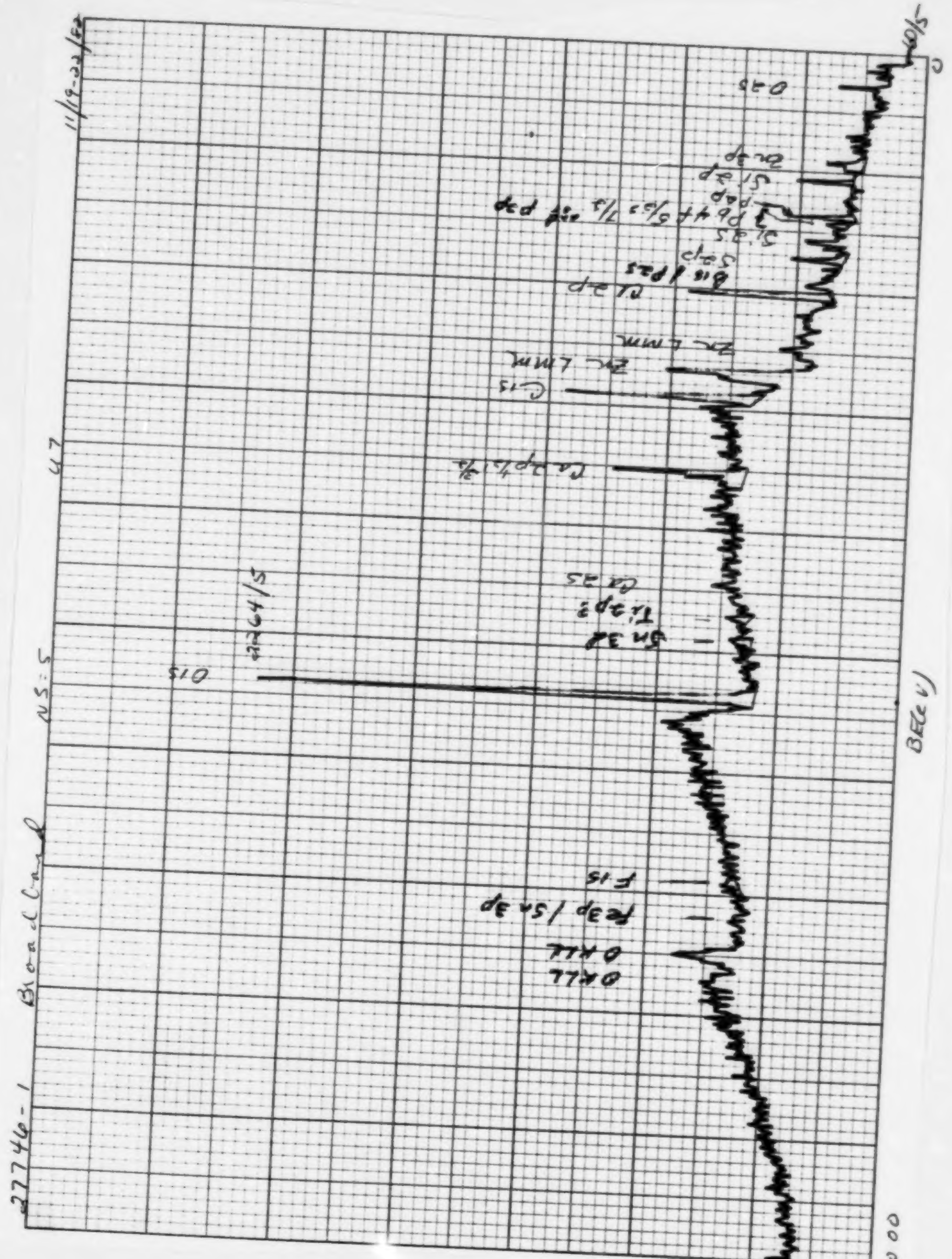

21369
Broad band
NS=5
11/16/82
1000
0
BE(eV)
157/5
535/5
1376/5
Ca LMM
OKLL
OKLL
O 1s
Sn 3d 3/2, 5/2 ?
Ca 2s
Ag 3d 3/2, 5/2
} Ca 2p 1/2, 3/2
C 1s
Na KLL
S 2s
P 2p
S 2p
P 2s
Ca 3s
O 2s + Ca 3p


21370
Broadband
NS=5
11/16/82
1496/5
O 1s
V 2p
Cr 2p3/2
Ca 2s
Ca 2p3/2,1/2
C 1s
Na KLL
S 2s
P 2p?
S 2p
Si 2s
Al 2s
Si 2p
Mg 2s
Al 2p
Mg 2p
Ca 3s
O 2s + Ca 3p
OKLL
OKLL
174/5
345
1000
0
B.E.(eV)

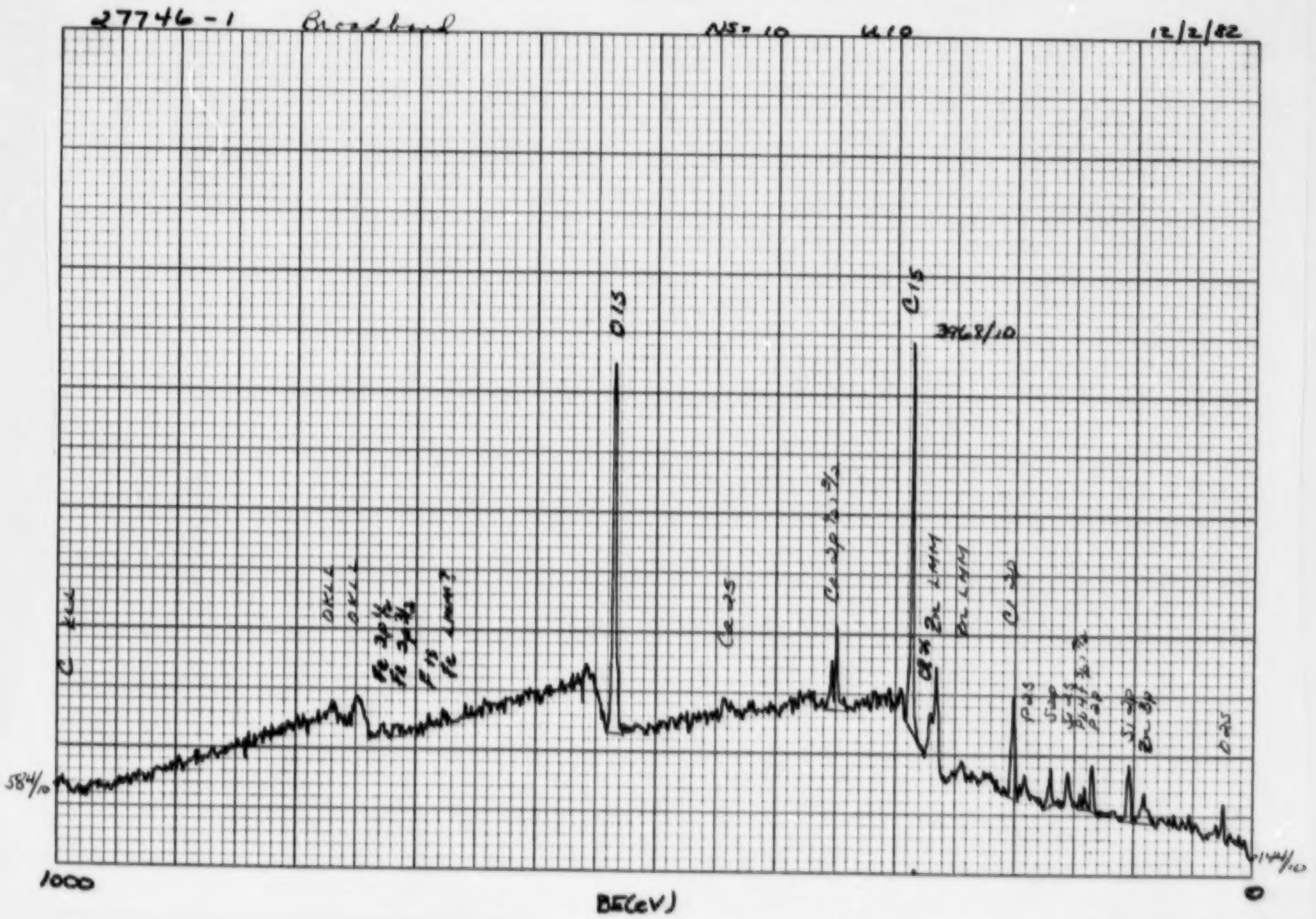

37745-1
Bread board
NS=5
U3
11/19/82
1000
0
BE(eV)
OKLL
F1s
O 1S
Ca 2s
Ca 2p1/2,3/2
Zn LMM
C1s
Zn LMM
Zn LMM
Cl 2p
P2s
S 2p
Pb 4f 5/2, 7/2
Zn 3s
P2p
Zn 3p
Ca 3s
O2s + Ca 3p
Pb Zn 3d

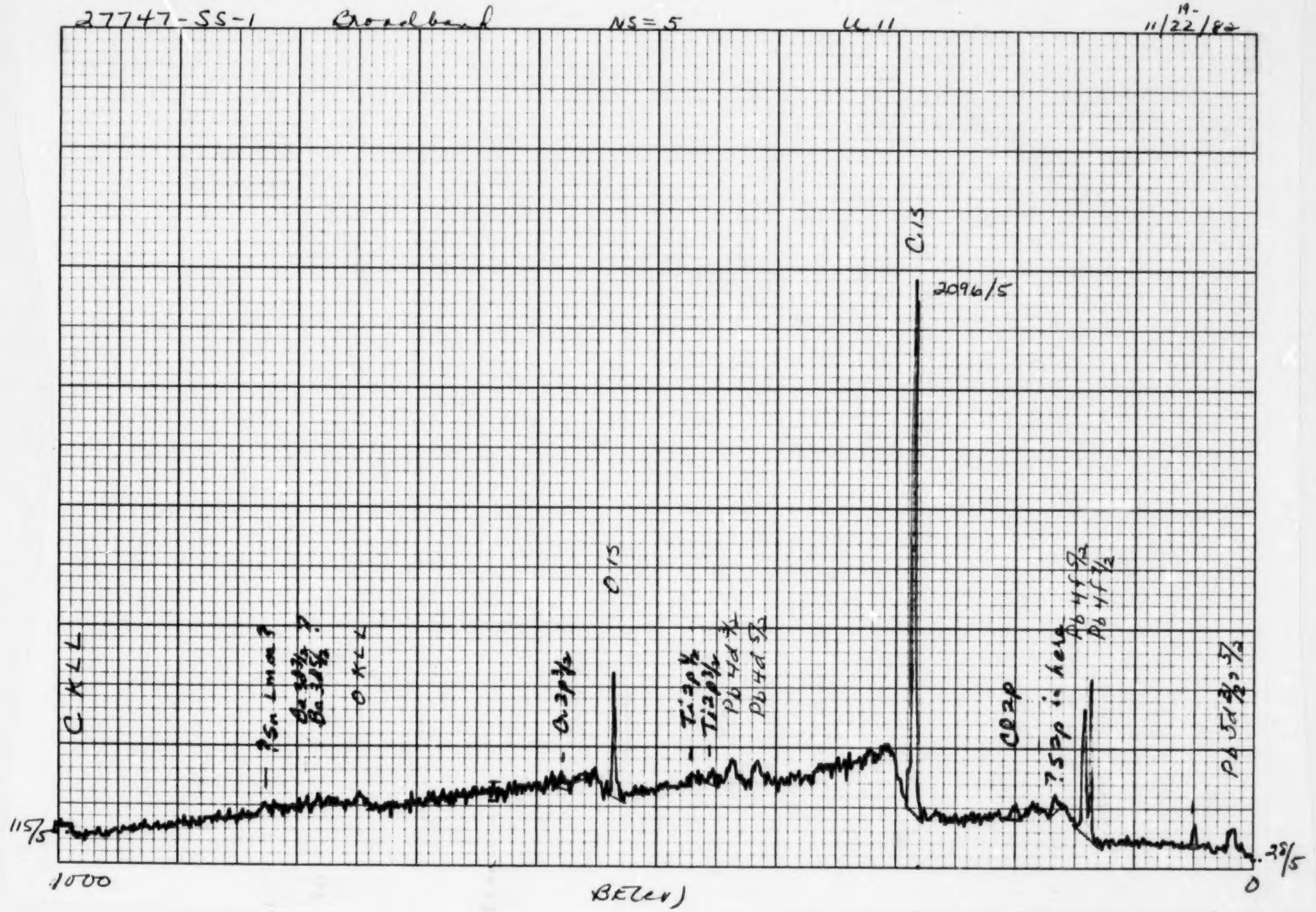

27745-1
Broadband
NS=5
4.9
11/19/82
O KLL
2000/5
O KLL
Sn 3p?
F 1s
V 2p 3/2 1/2?
Sn 3d?
Ca 2s
Pb 4p 1/2
Pb 4d 3/2
Ca 2p 1/2 3/2
Zn LMM
C 1s
Zn LMM
Zn LMM
Cl 2p
P 2s
S 2p
Si 2s
Pb 4f 5/2 7/2
/P 2p
ST 2p
Zn 3p
Ca 3s
O 2s / Ca 3p
Zn 3p
440/5
90/5
1000
BE(eV)
0

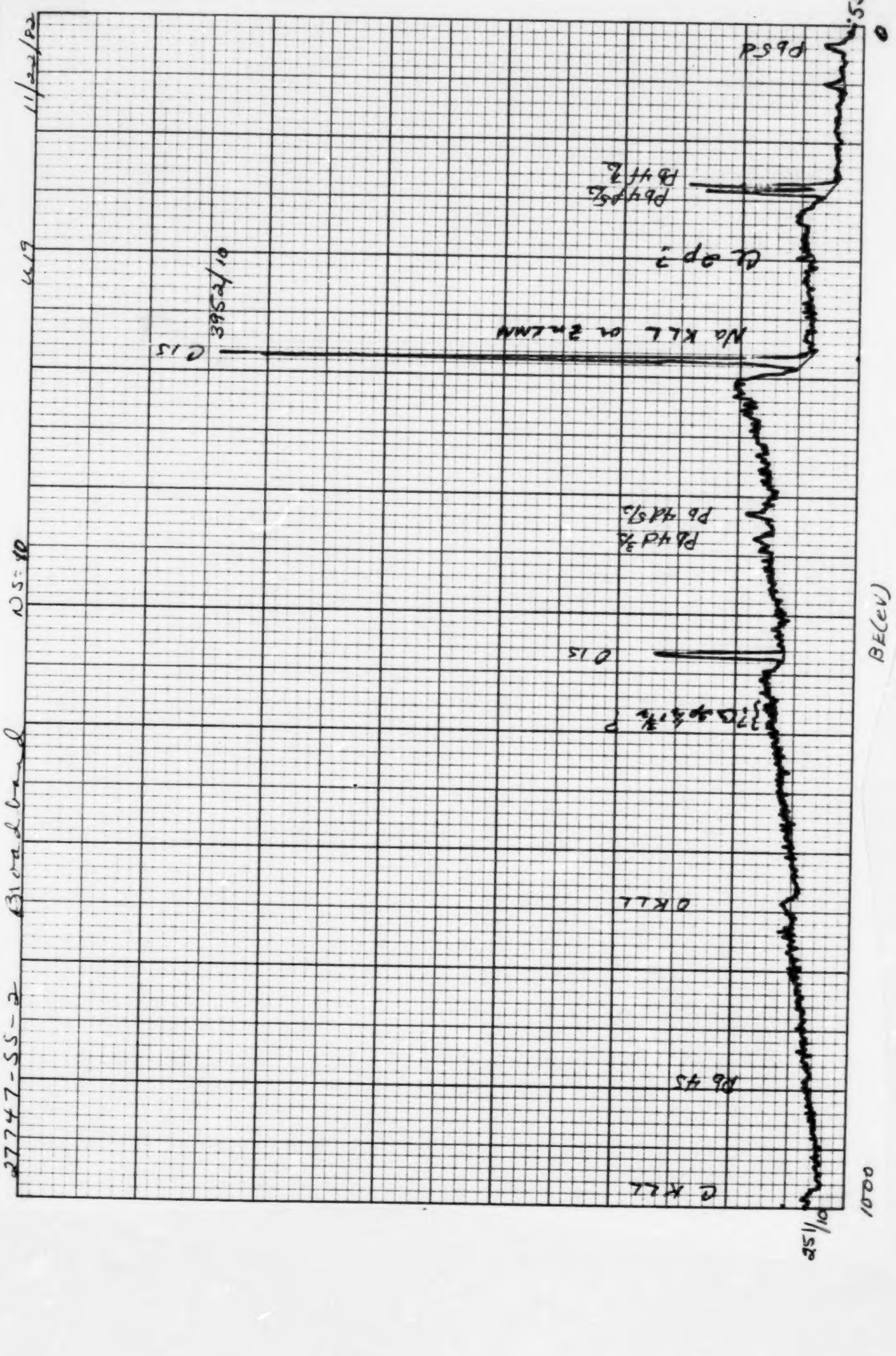

27745-1 Broadband
NS=10
U9
12/1-2/82
O KLL
O KLL
O 1s
Sn 3d 5/2, 3
Ca 2s
Ca 2p 1/2, 3/2
Zn LMM
C 1s
Zn LMM
Zn LMM
Cl 2p
P 2s
S 2p
Pb 4f 5/2
Pb 4f 7/2
P 2p
Si 2p
Zn 3p
O 2s + Ca 3p
Zn 3d
1000
BE(eV)
0

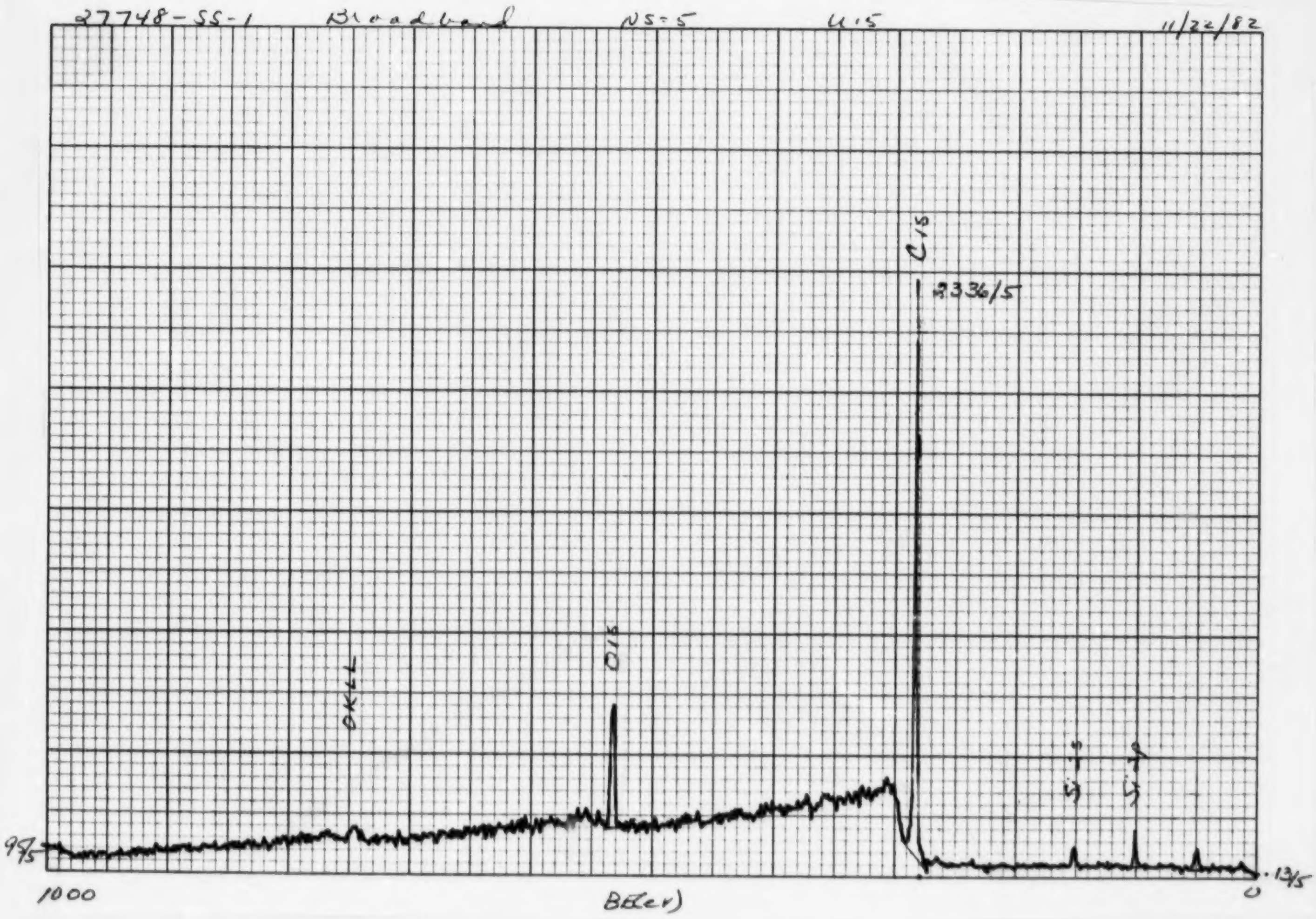


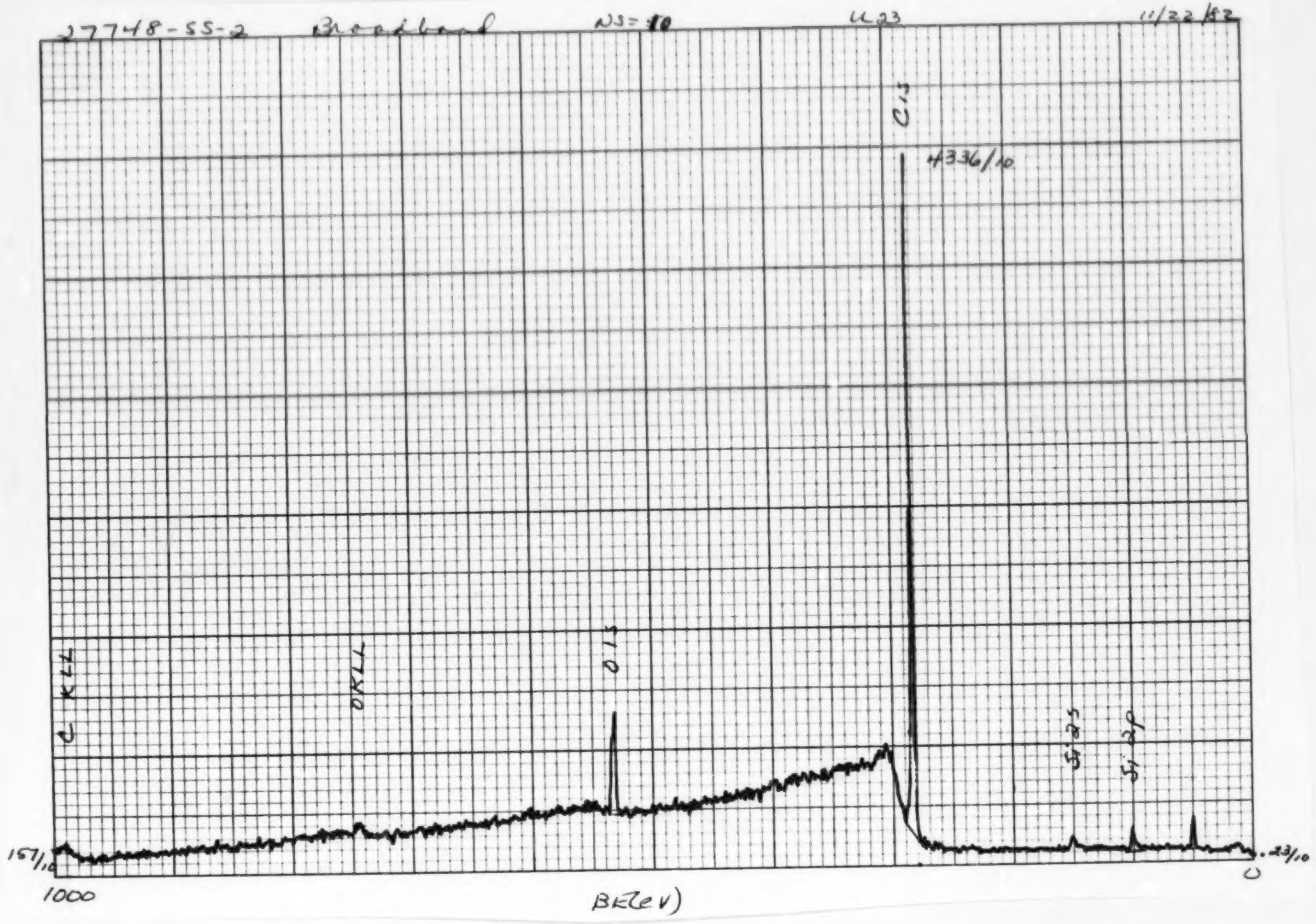
27746-1
Broad Scan
NS:5
4.7
11/19-22/82
O KLL
O KLL
Fe 3p / Sn 3p
F 1s
O 1s
2264/s
Sn 3d
Ti 2p?
Ca 2s
Ca 2p 1/2 3/2
C 1s
Zn LMM
Zn LMM
Cl 2p
Bi 4f / P 2s
S 2p
Si 2s
Pb 4f 5/2 7/2 of P 2p
P 2p
Si 2p
Zn 3p
O 2s
BE(eV)
1000
0
10/s
30/s

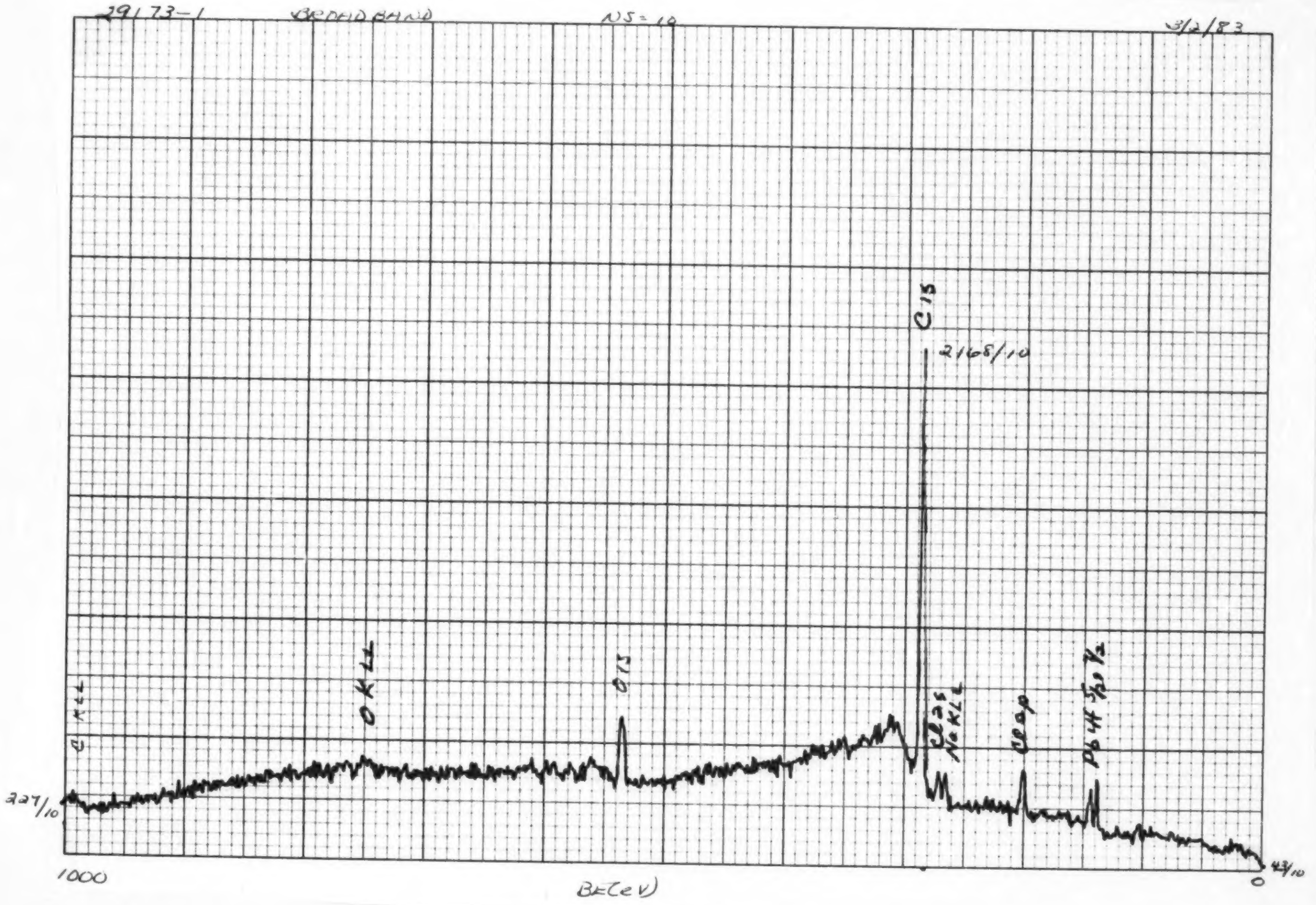

27746-1
Broadband
NS=10
W10
12/2/82
O1S
C1S
3968/10
C KLL
OKLL
OKLL
Fe 2p1/2
Fe 2p3/2
F 1s
Fe LMM?
Ca 2s
Ca 2p1/2,3/2
Ca x
Zn LMM
Zn LMM
Cl 2p
P 2s
S 2p
Si 2s
Pb 4f5/2,7/2
P 2p
Si 2p
Zn 3p
O 2s
584/10
144/10
1000
0
BE(eV)

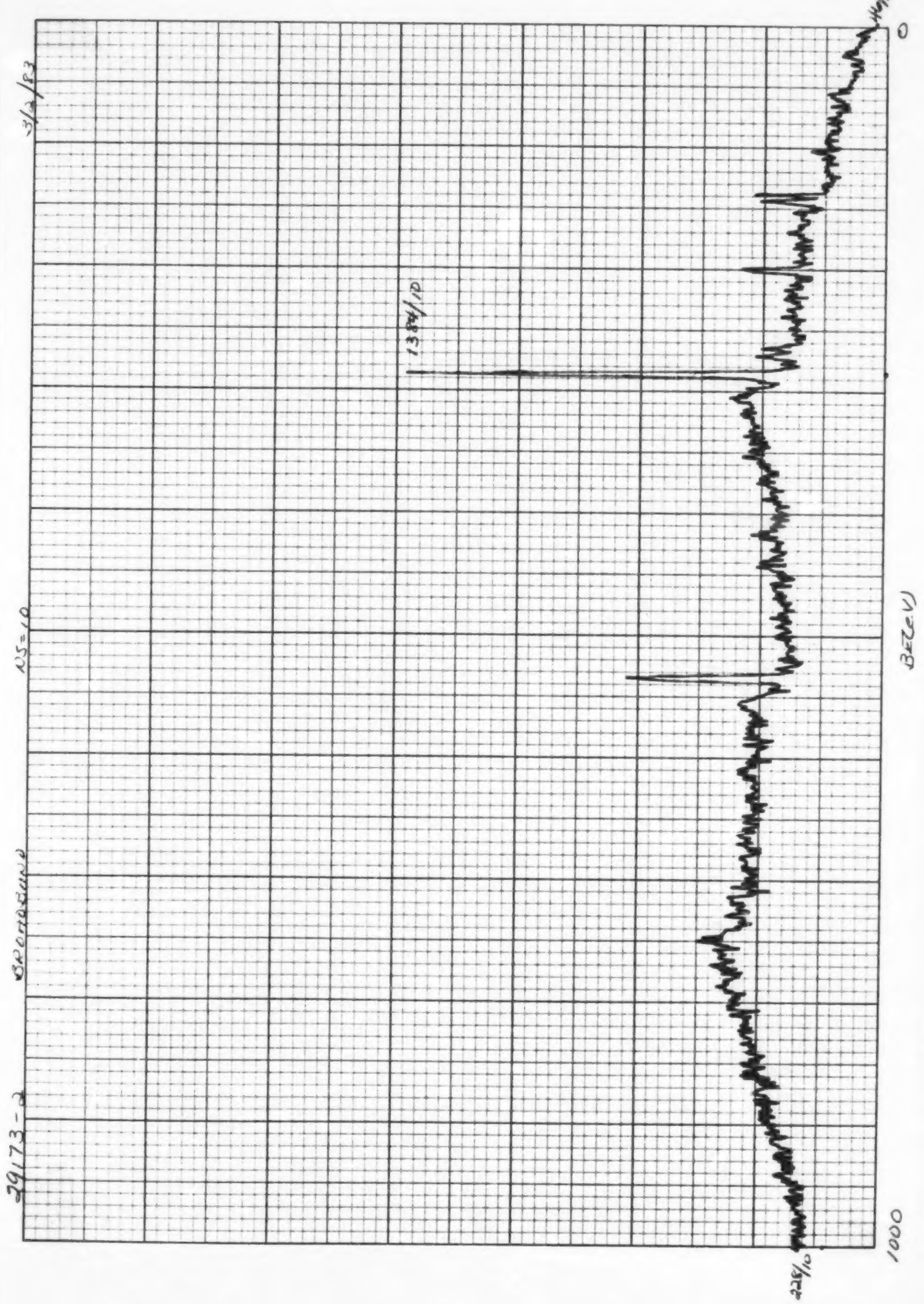

27747-SS-1
Broadband
NS=5
U 11
19-11/22/82
C KLL
?Sn LMM ?
Ba 3d3/2 ?
Ba 3d5/2
O KLL
Ba 3p3/2
O 1s
Ti 2p1/2
Ti 2p3/2
Pb 4d 3/2
Pb 4d 5/2
C 1s
2096/5
Ce 2p
?5p is here
Pb 4f 5/2
Pb 4f 7/2
Pb 5d 3/2, 5/2
115/5
25/5
1000
0
BE(eV)

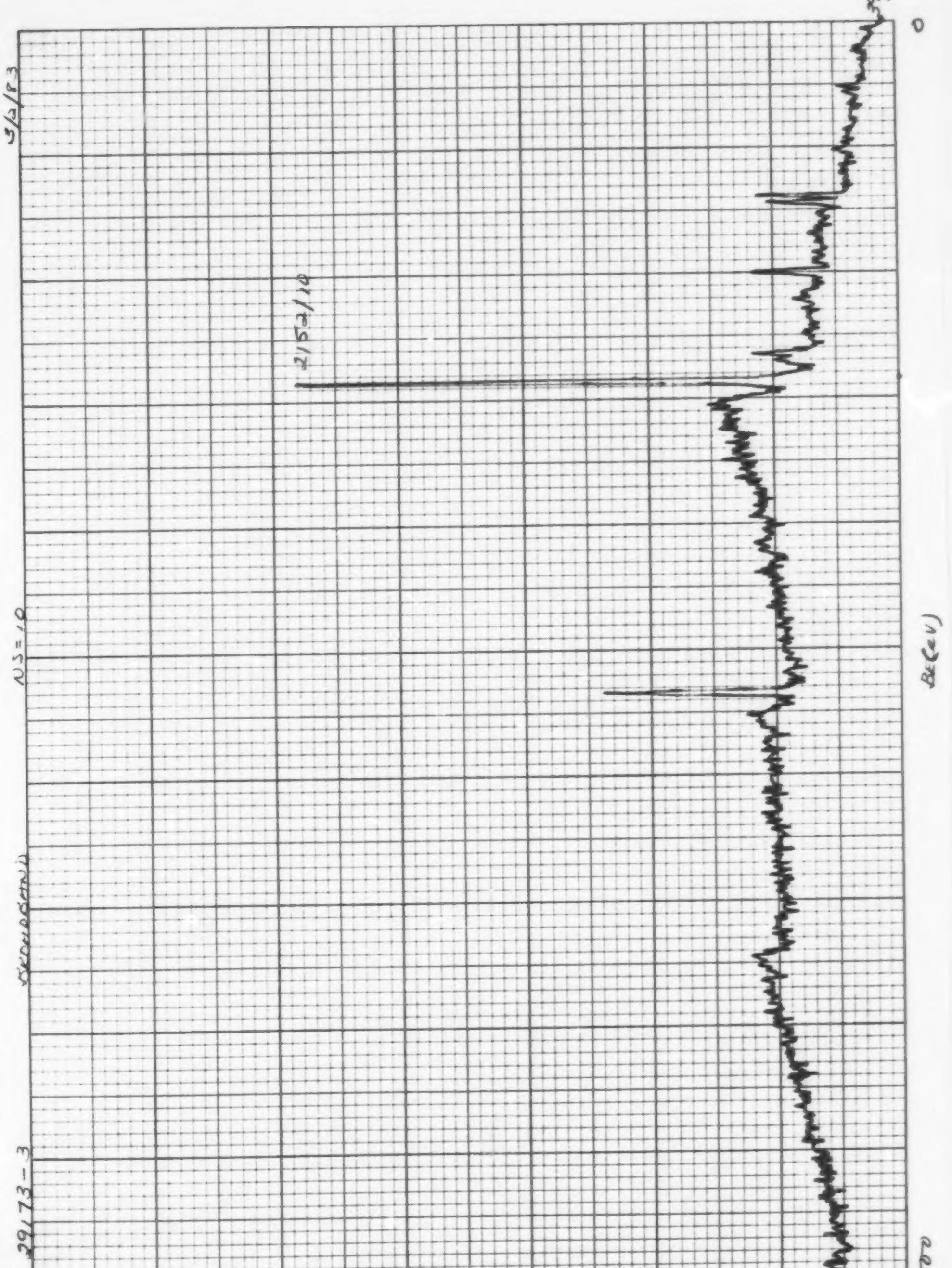

27747-SS-2
Broadband
NS: 10
4/19
11/22/82
53/10
0
Pb 5d
Pb 4f5/2
Pb 4f7/2
Cl 2p ?
Na KLL or Zn LMM
O 1s
395e2/10
Pb 4d3/2
Pb 4d5/2
O 1s
Pb 4p3/2 ?
O KLL
Pb 4S
C KLL
251/10
1000
BE(eV)

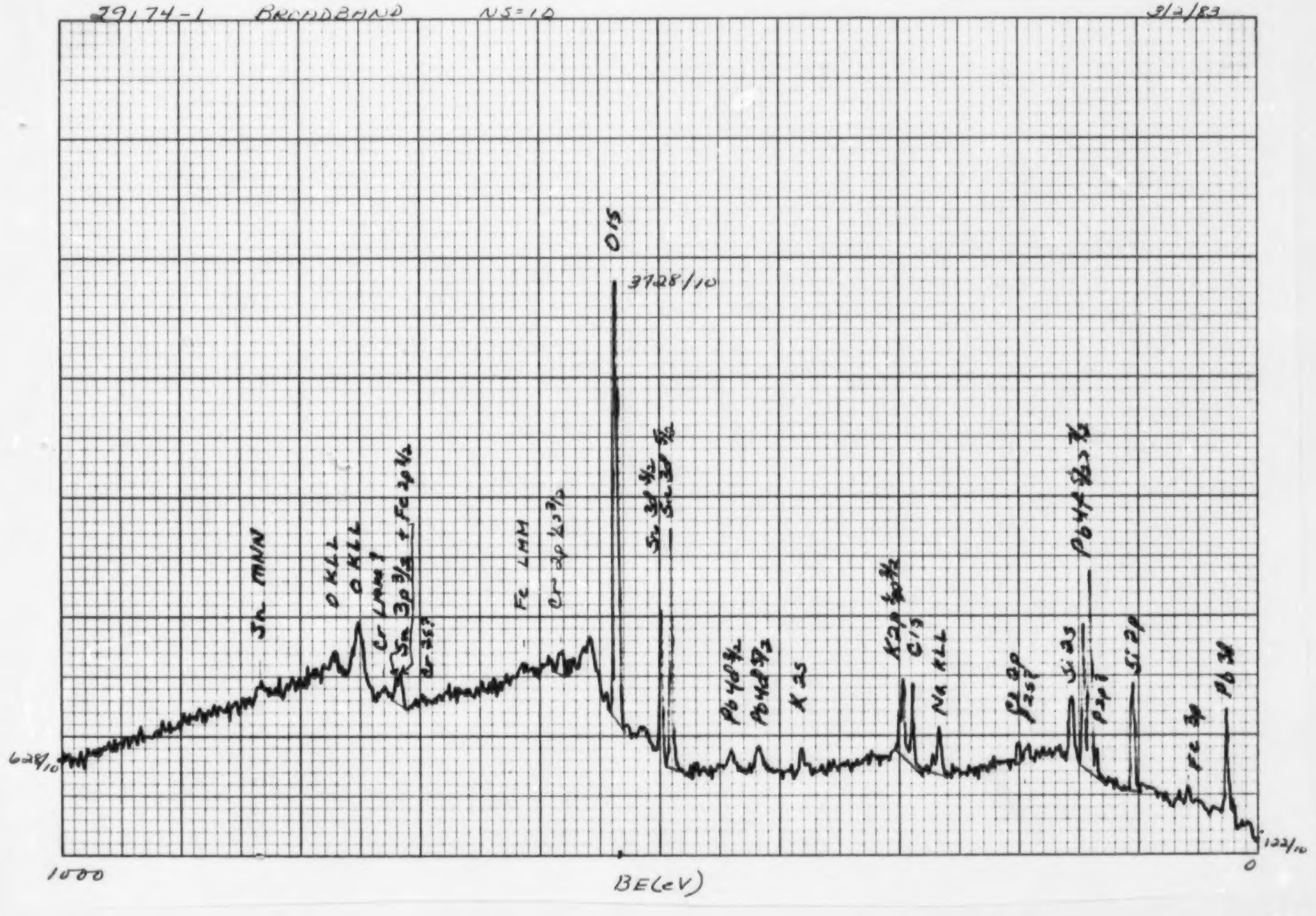

27748-SS-1
Broadband
NS=5
U:5
11/22/82
C1s
2336/5
O1s
OKLL
Si 2s
Si 2p
97/5
13/5
1000
BE(ev)
0

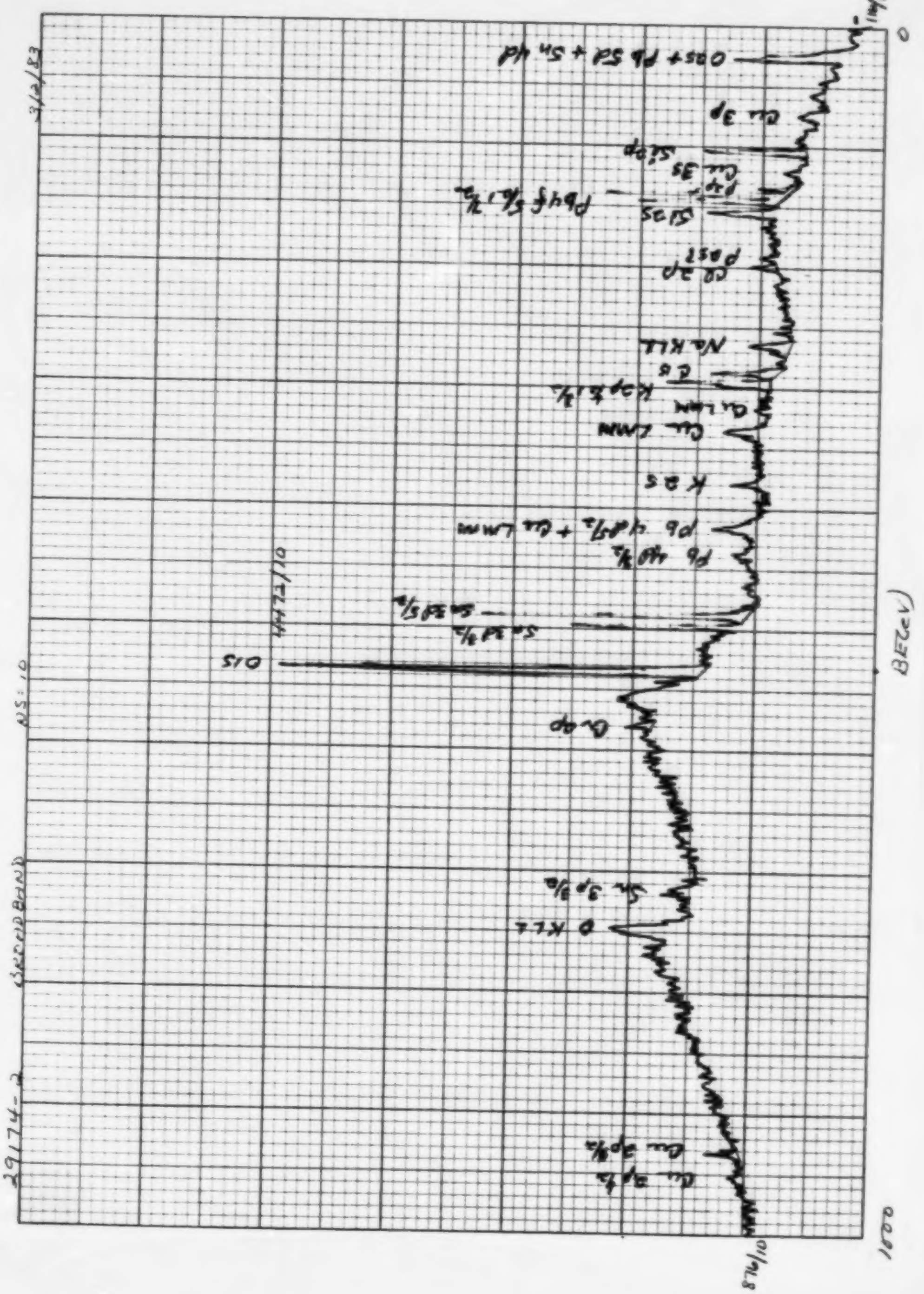

27748-SS-2
Broadband
NS=10
U23
11/22/82
C1s
4336/10
O1s
OKLL
C KLL
Si 2s
Si 2p
157/10
.23/10
1000
0
BE(eV)


29173-1
BROAD BAND
NS=10
3/2/83
C1s
2168/10
O1s
OKLL
C KLL
Cl2s
NaKLL
Cl2p
Pb4f 5/2 7/2
227/10
43/10
1000
0
BE(eV)

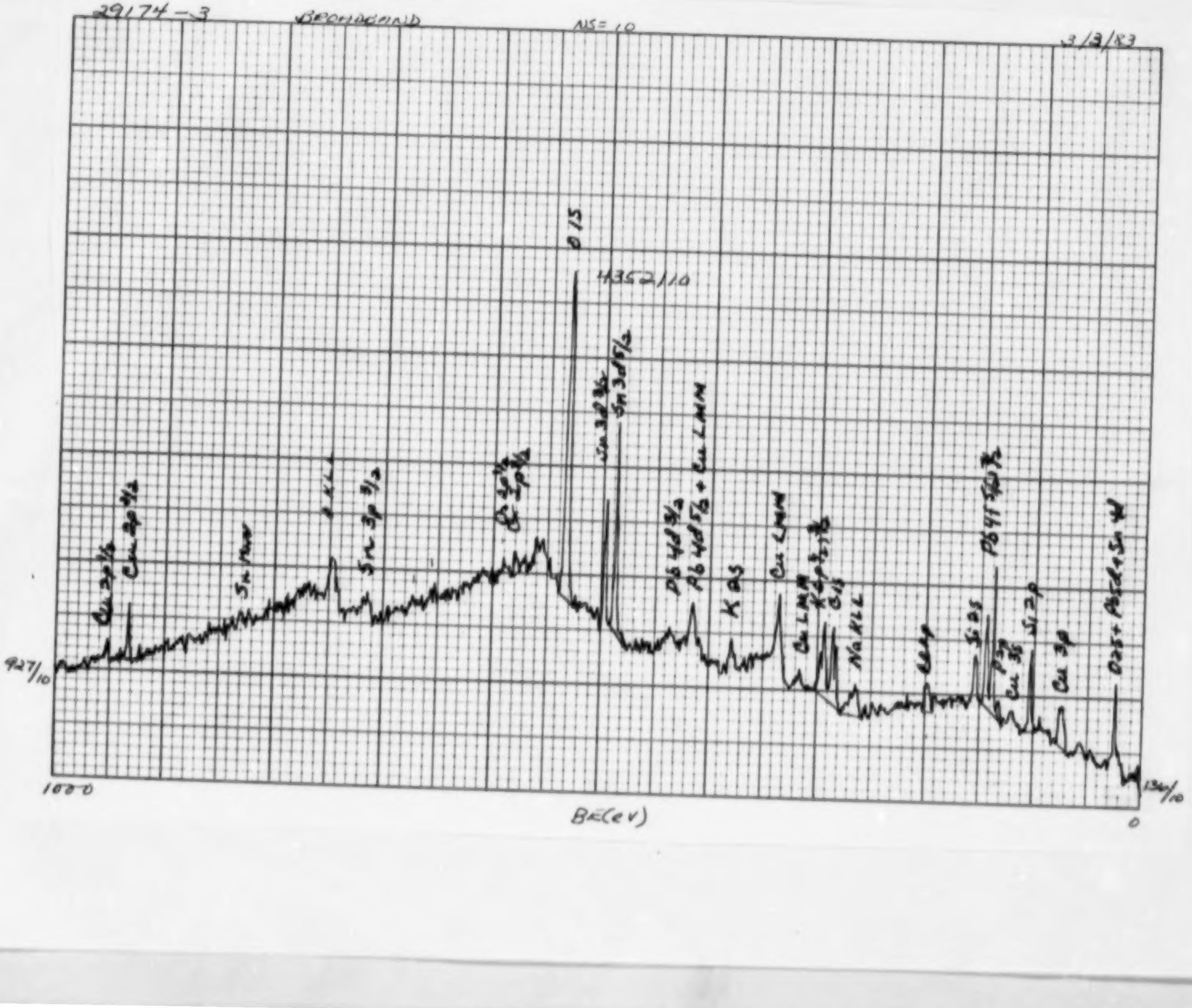

29173-2
BROMOFORM
NS=10
3/2/83
1384/10
144/10
0
BE(eV)
1000
228/10

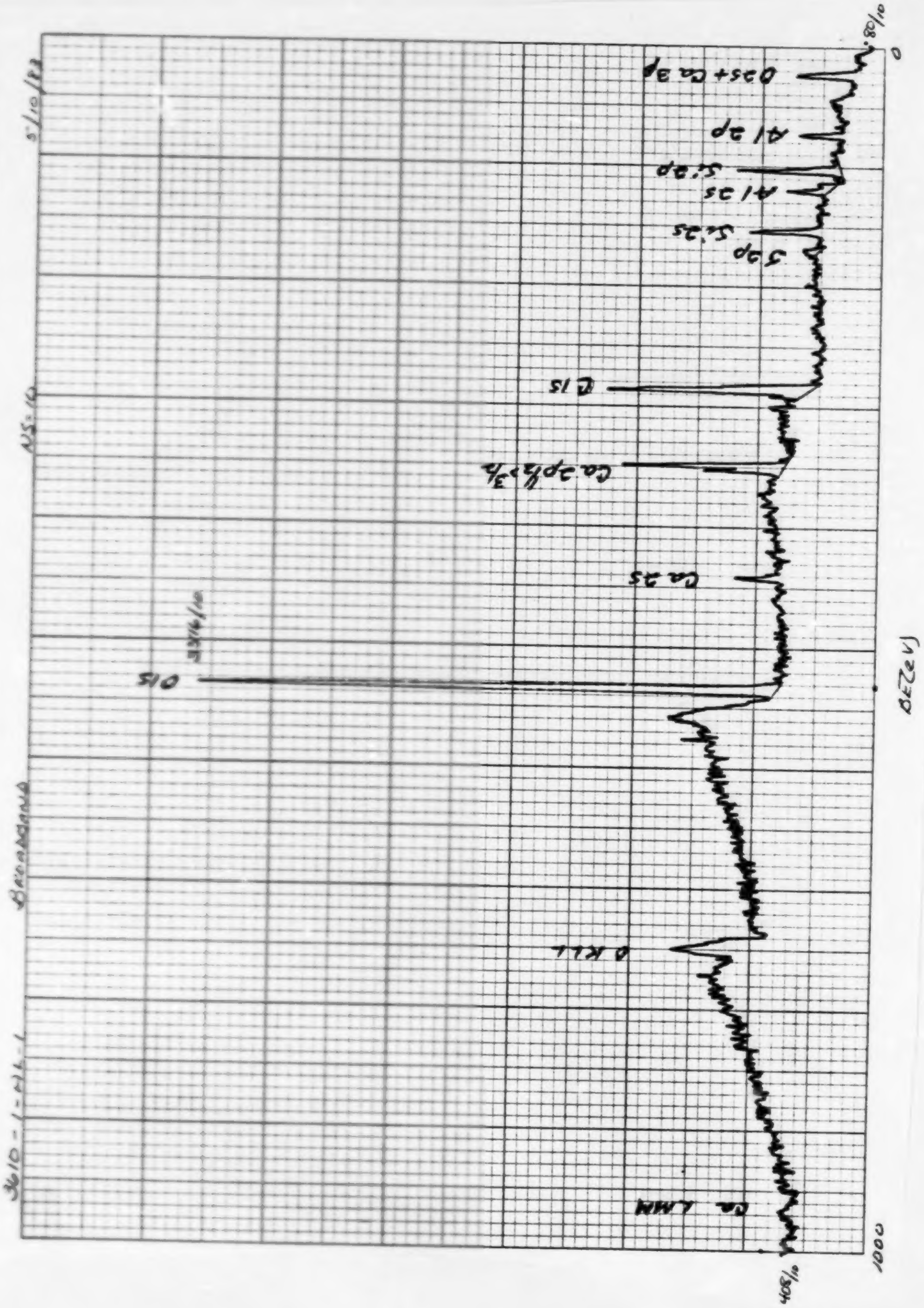

29173-3
BACKGROUND
NS=10
3/2/83
2152/10
253/10
39/10
1000
0
BE(eV)

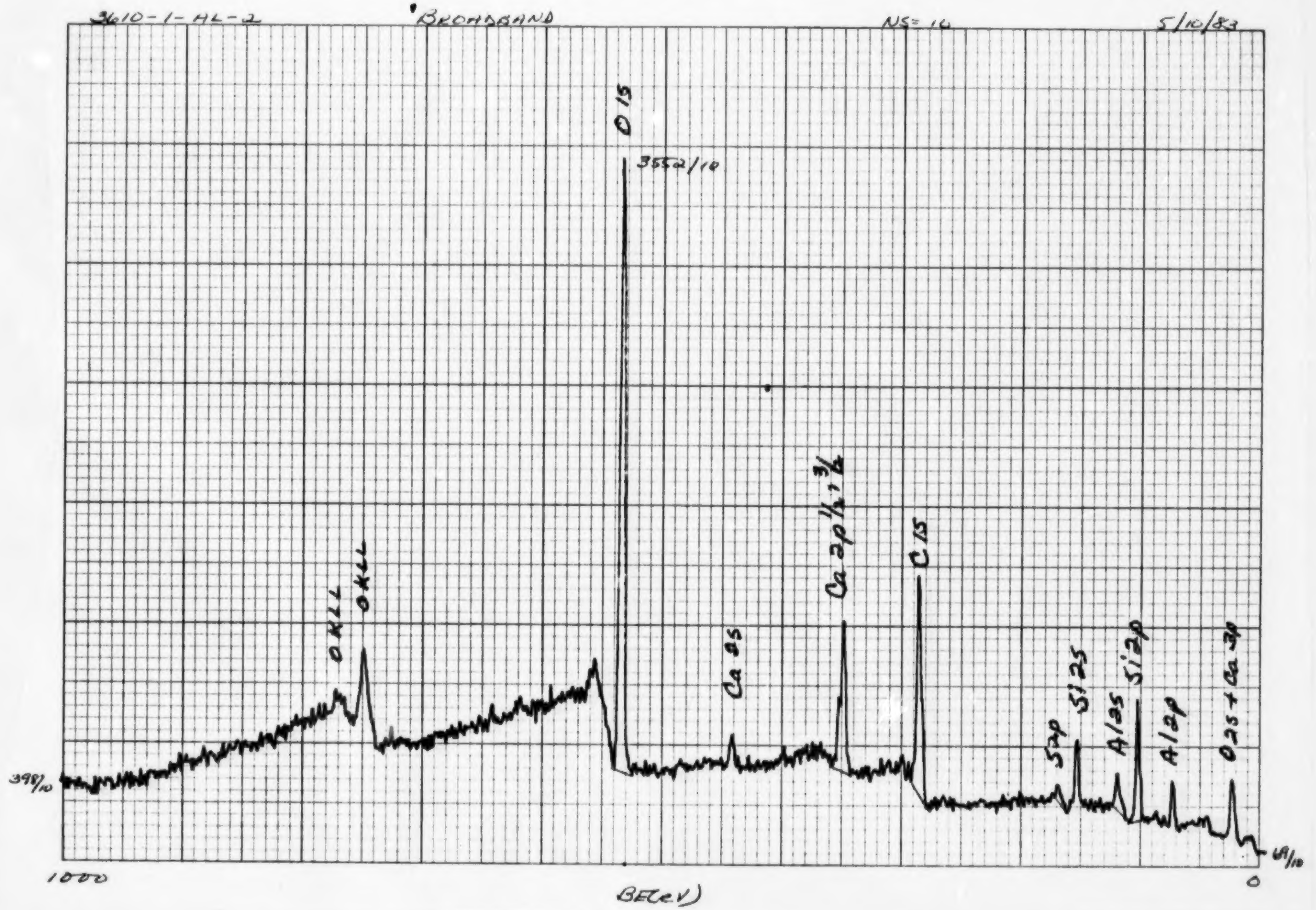

29174-1 BROADBAND NS=10
3/2/83
O1s
3728/10
628/10
122/10
Sn MNN
O KLL
O KLL
Cr LMM ?
Sn 3p 3/2 + Fe 2p 1/2
Cr 2s ?
Fe LMM
Cr 2p 1/2 3/2
Sn 3d 3/2
Sn 3d 5/2
Pb 4d 3/2
Pb 4d 5/2
K 2s
K 2p 1/2 3/2
C 1s
Na KLL
Pb 4f 5/2 7/2
Cl 2p
Cl 2s
Si 2s
P 2p ?
Si 2p
Fe 3p
Pb 5d
1000
BE(eV)
0

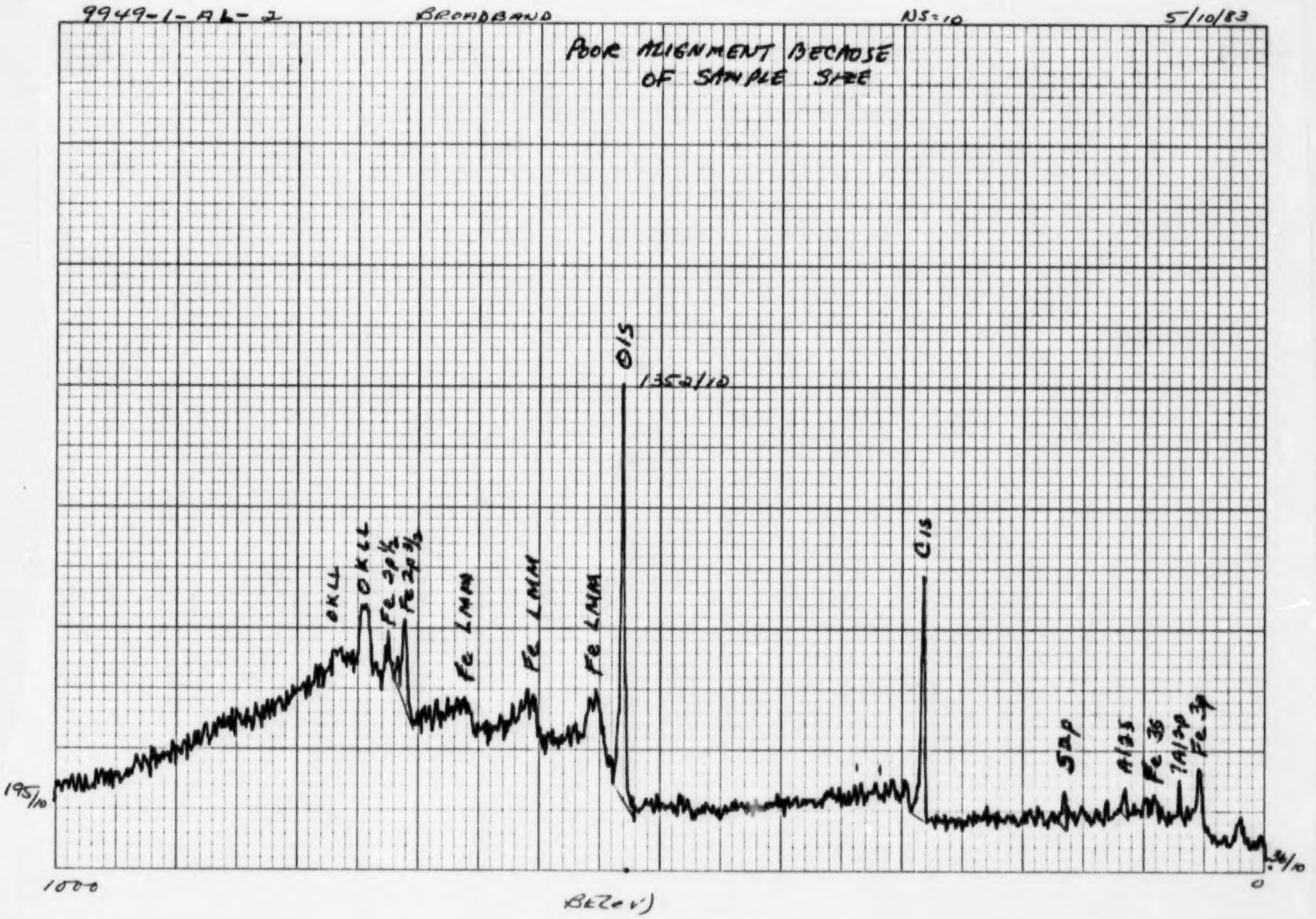


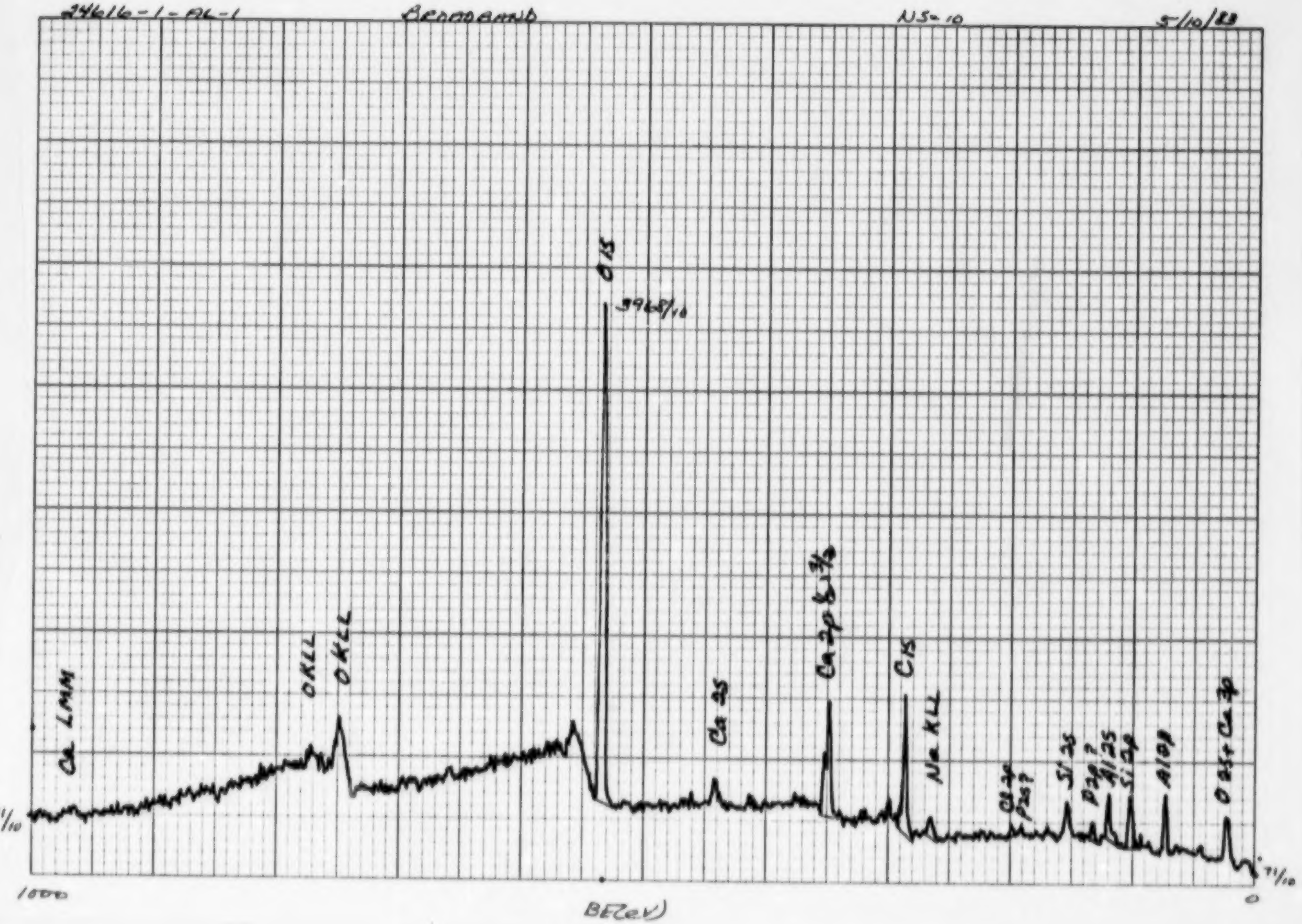
29174-2
SPEEDBAND
NS:10
3/2/83
BE(eV)
0
1000
1114/10
876/10
4473/10
O2s + Pb 5d + Sn 4d
Cu 3p
Cu 3s
Si 2p
Pb 4f 5/2, 7/2
Si 2s
Cl 2p
P 2s?
Na KLL
C 1s
Cu LMM
K 2p 1/2, 3/2
Cu LMM
K 2s
Pb 4d 5/2 + Cu LMM
Pb 4d 3/2
Sn 3d 5/2
Sn 3d 3/2
O 1s
Cu 4p
Sn 3p 3/2
O KLL
Cu 2p 3/2
Cu 2p 1/2

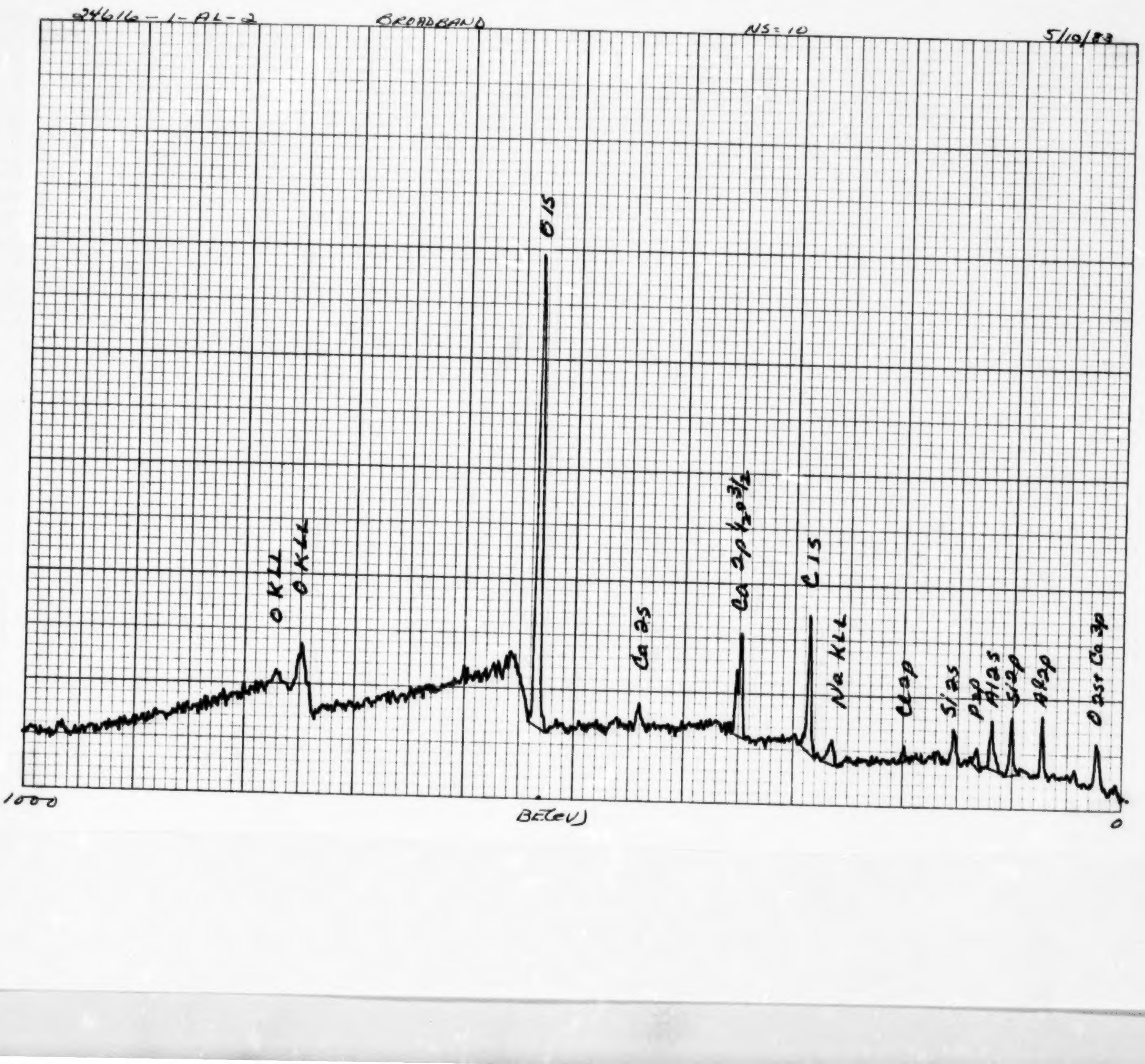

29174-3
BROADBAND
NS=10
3/3/83
O 1S
4352/10
Sn 3d3/2
Sn 3d5/2
Pb 4d3/2
Pb 4d5/2 + Cu LMM
K 2s
Cu LMM
Cu LMM
K 2p1/2,3/2
C 1s
Na KLL
Cl 2p
Si 2s
Pb 4f5/2,7/2
P 2p
Cu 3s
Si 2p
Cu 3p
O 2s + Pb5d + Sn 4d
Cu 2p1/2
Cu 2p3/2
Sn MNN
O KLL
Sn 3p3/2
Cr 2p1/2
Cr 2p3/2
927/10
1340/10
1000
0
BE(eV)

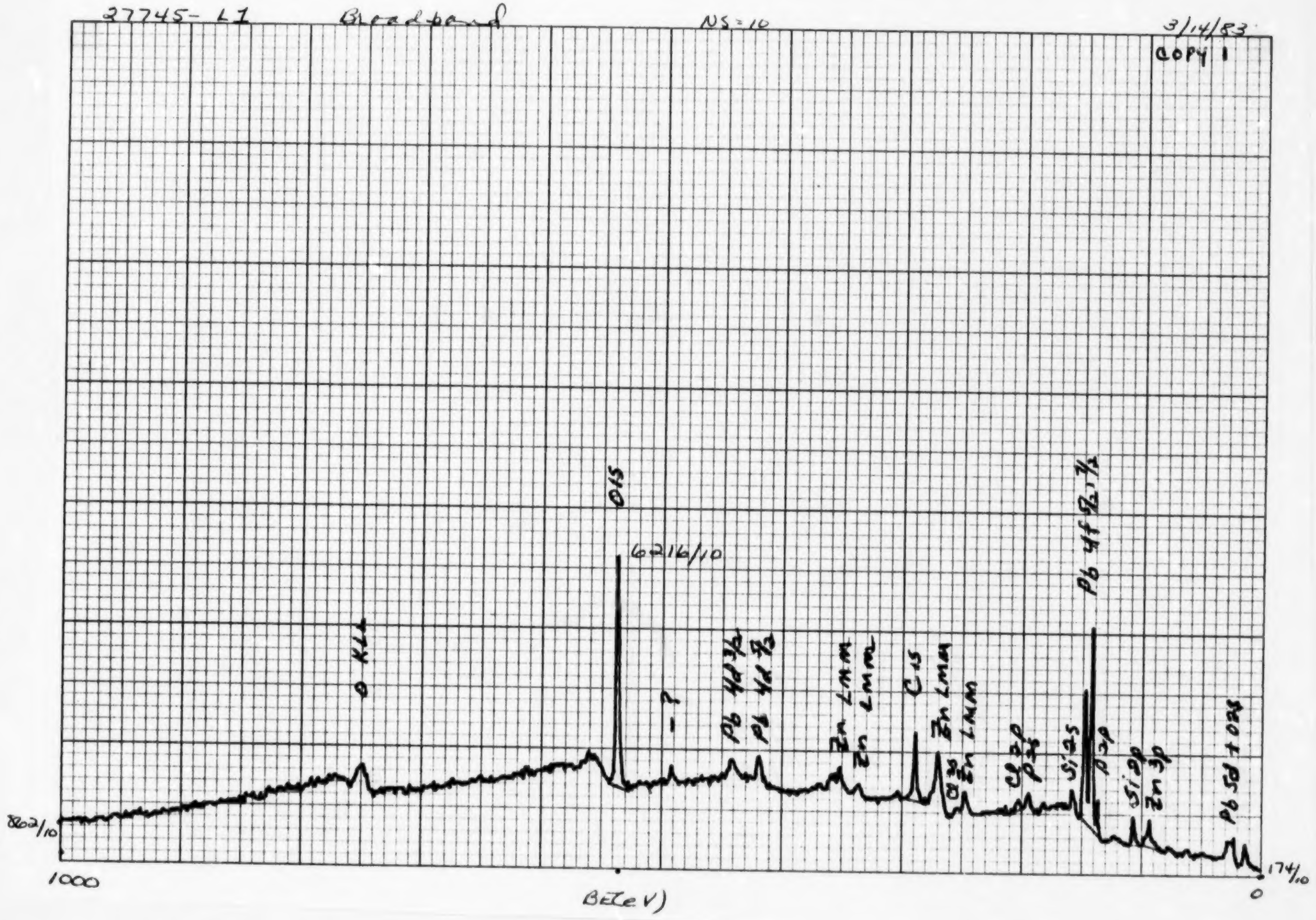

3610-1-NL-1
Brennand
NS=10
5/10/83
BE(eV)
0
1000
80/10
408/10
O 2s + Ca 3p
Al 2p
Si 2p
Al 2s
Si 2s
S 2p
C 1s
Ca 2p1/2,3/2
Ca 2s
O 1s
3316/10
O KLL
Ca LMM

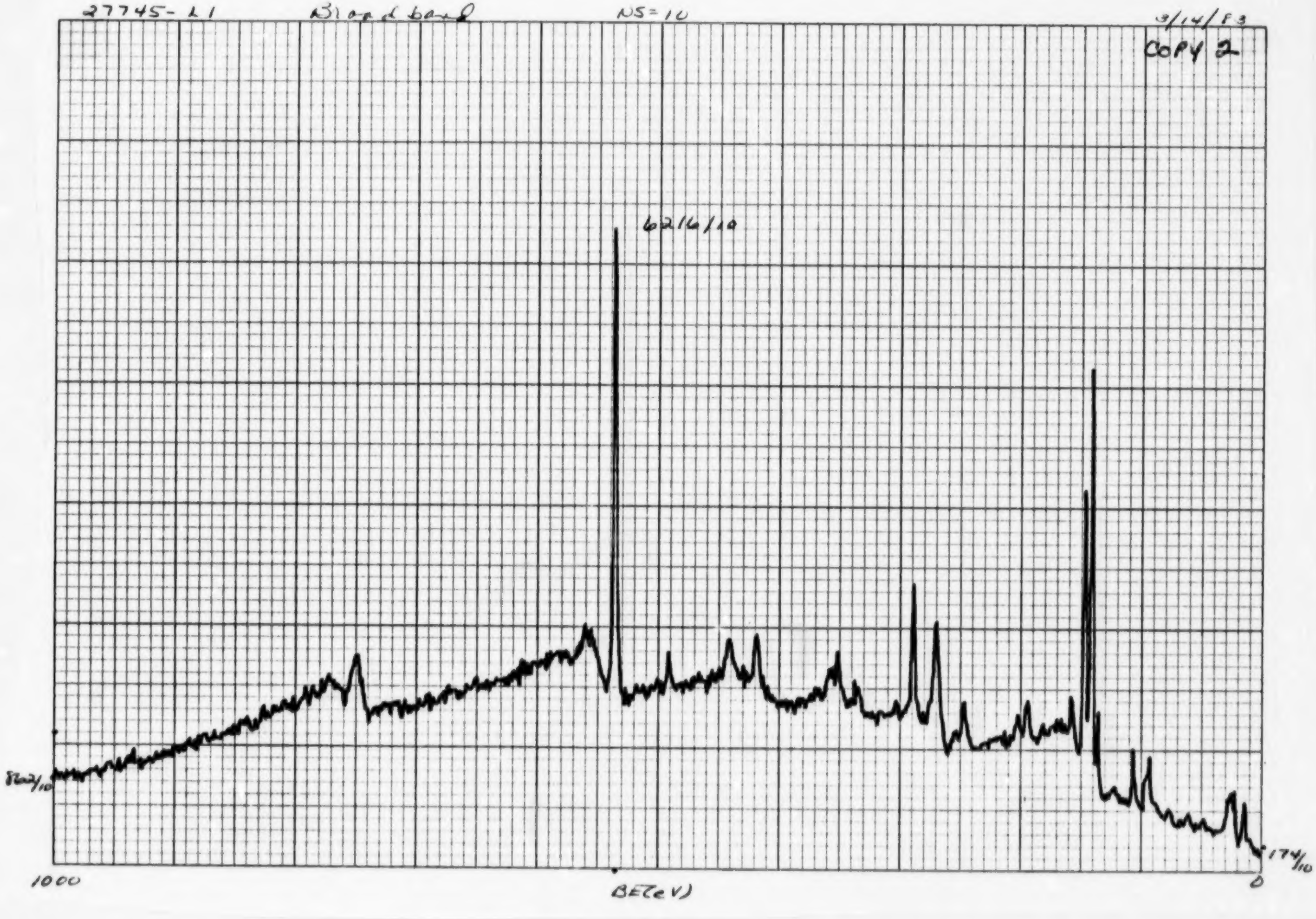

3610-1-AL-2
'BROADBAND
NS=16
5/10/83
O 1s
3552/10
OKLL
OKLL
Ca 2s
Ca 2p1/2,3/2
C 1s
S2p
Si2s
Al2s
Si2p
Al2p
O2s + Ca 3p
398/10
69/10
1000
BE(eV)
0

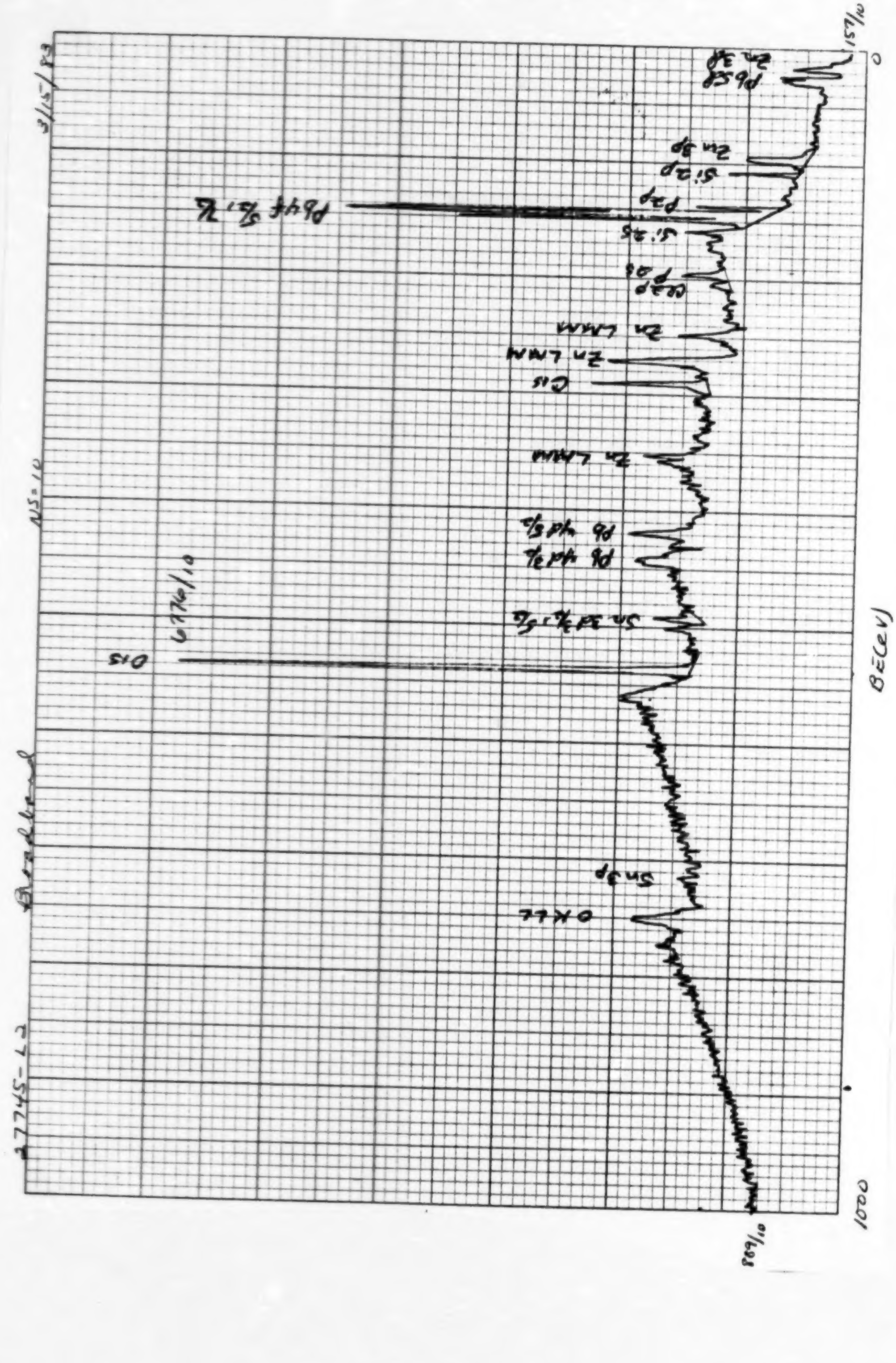

9949-1-AL-2
BROADBAND
NS=10
5/10/83
POOR ALIGNMENT BECAUSE OF SAMPLE SIZE
OKLL
OKLL
Fe 2p½
Fe 2p3/2
Fe LMM
Fe LMM
Fe LMM
O1s
1352/10
C1s
S2p
Al2s
Fe 3s
?Al2p
Fe 3p
195/10
34/10
1000
BE(eV)
0


24616-1-AL-1
BROADBAND
NS=10
5/10/83
O 1S
3968/10
Ca LMM
OKLL
OKLL
Ca 2S
Ca 2p & 1/2
C1S
Na KLL
Ca 3S
P2S?
Si 2S
P2p?
Al 2S
Si 2p
Al 2p
O 2S + Ca 3p
411/10
71/10
1000
BE(eV)
0

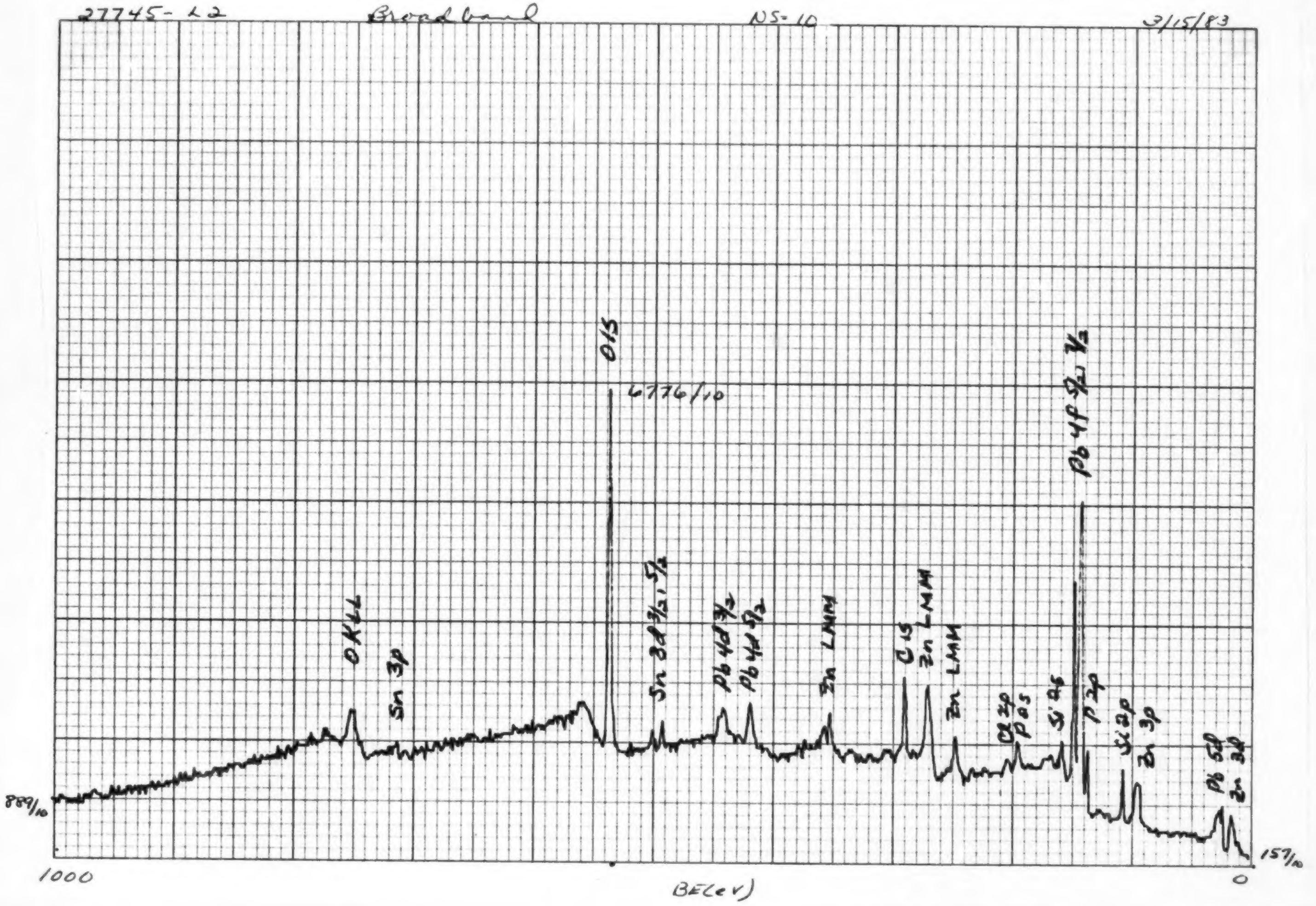

24616-1-AL-2
BROADBAND
NS=10
5/10/83
O KLL
O KLL
O 1S
Ca 2s
Ca 2p ½,3/2
C 1S
Na KLL
Cl 2p
Si 2s
P 2p
Al 2s
Si 2p
Al 2p
O 2s+ Ca 3p
1000
BE(eV)
0

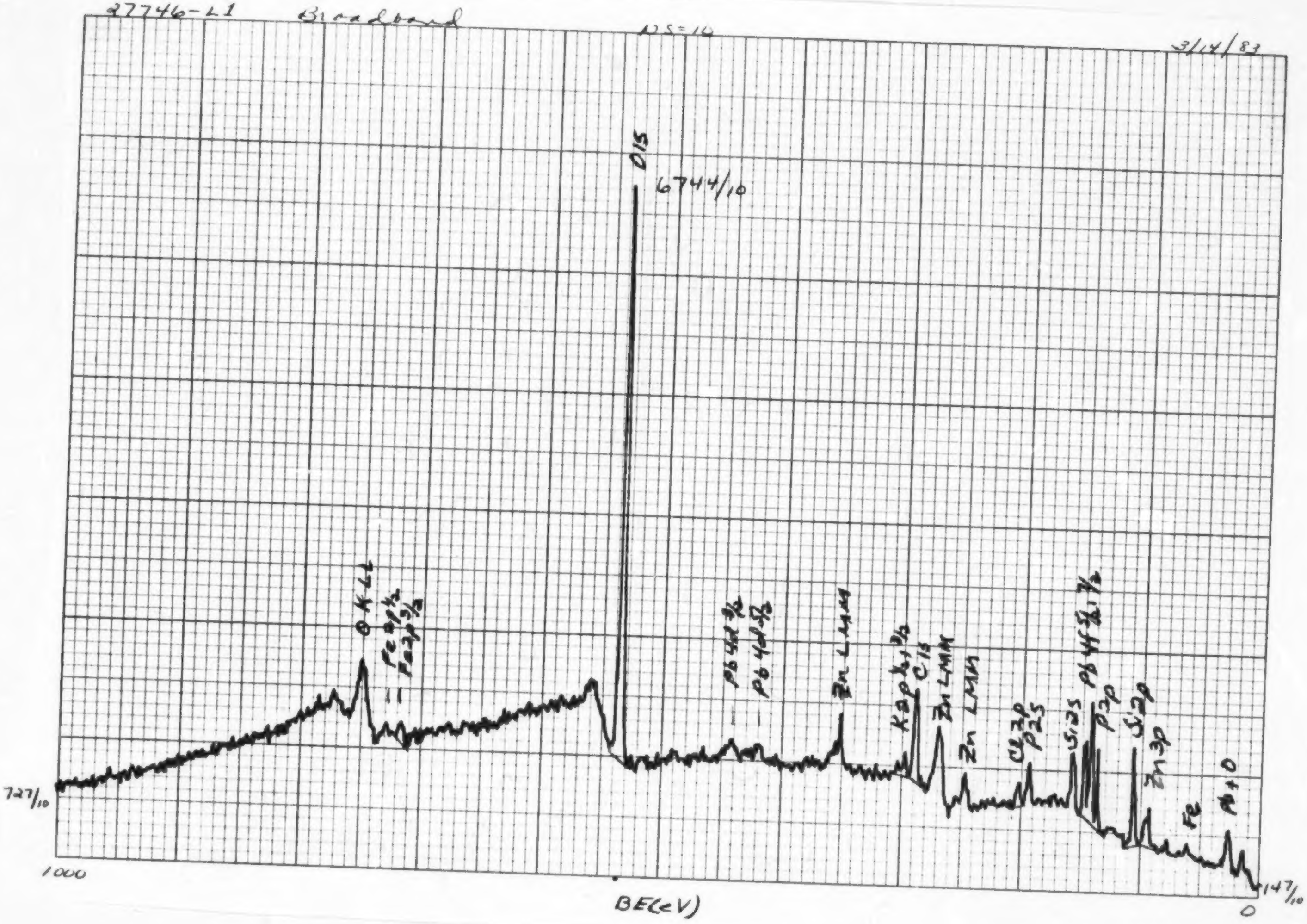

27745- L1
Broadband
NS=10
3/14/83
COPY 1
O KLL
O1s
6216/10
-?
Pb 4d3/2
Pb 4d5/2
Zn LMM
Zn LMM
C1s
Zn LMM
Cl2s
Zn LMM
Cl 2p
P 2s
Si 2s
Pb 4f 5/2, 7/2
P 2p
Si 2p
Zn 3p
Pb 5d + O2s
8802/10
174/10
1000
0
BE(eV)

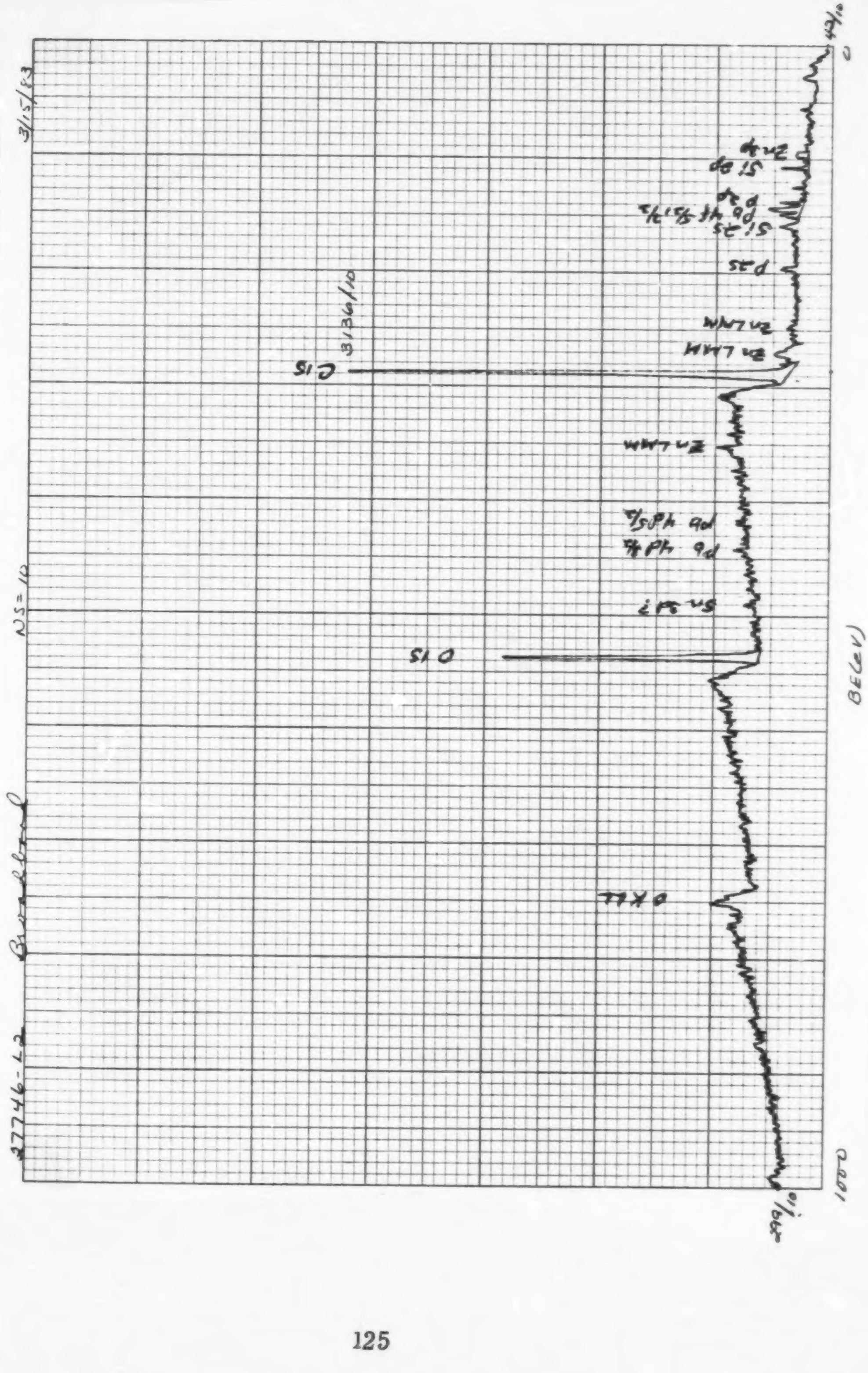

27745-21
Broad band
NS=10
3/14/83
COPY 2
6216/10
8002/10
174/10
1000
BE(eV)
0

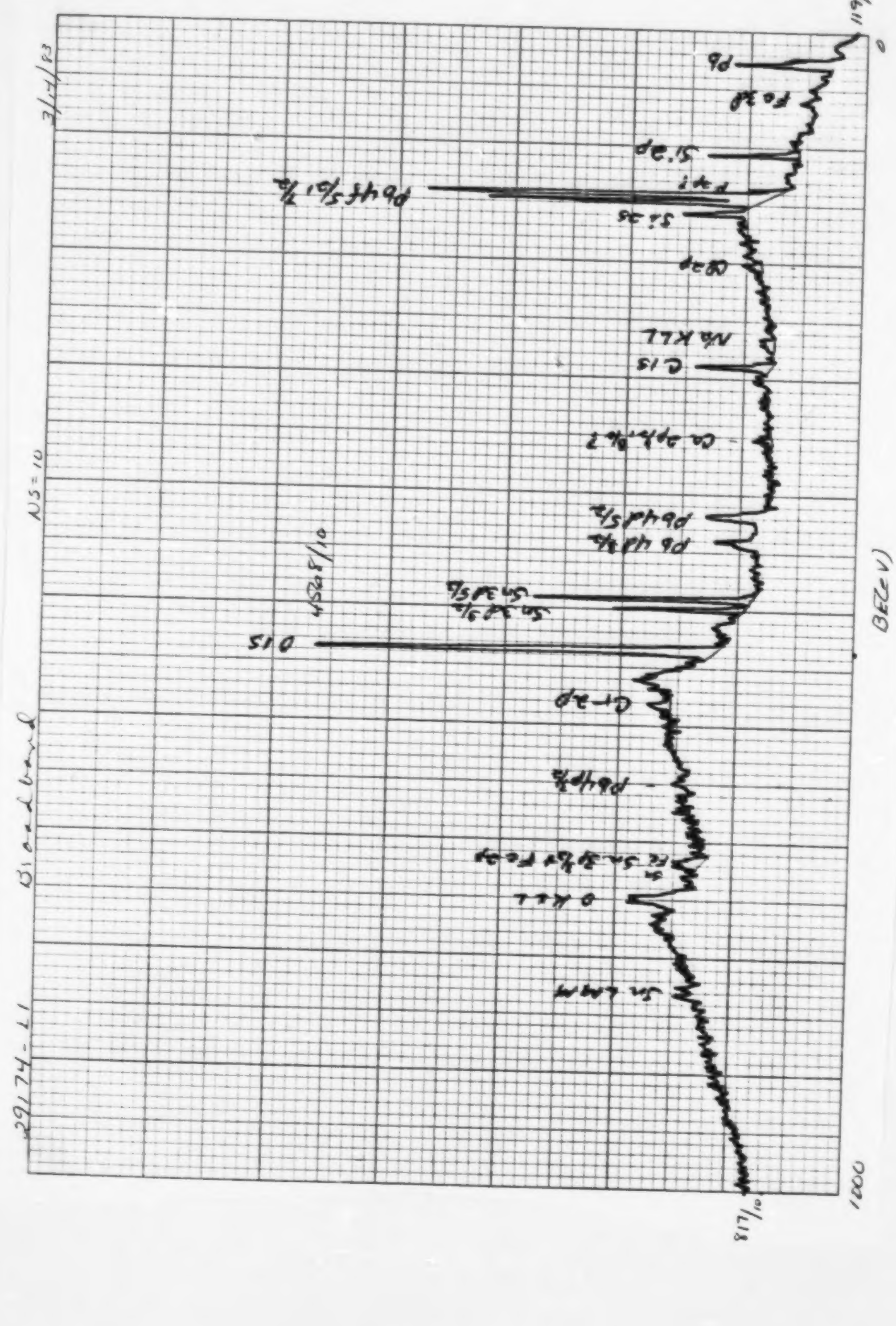

27745-L2
Broadband
NS=10
3/15/83
6776/10
O1s
OKLL
Sn 3p
Sn 3d 3/2, 5/2
Pb 4d 3/2
Pb 4d 5/2
Zn LMM
C1s
Zn LMM
Zn LMM
Cl 2p
P 2s
Si 2s
Pb 4f 5/2, 7/2
P 2p
Si 2p
Zn 3p
Pb 5d
Zn 3d
869/10
157/10
1000
0
BE(eV)

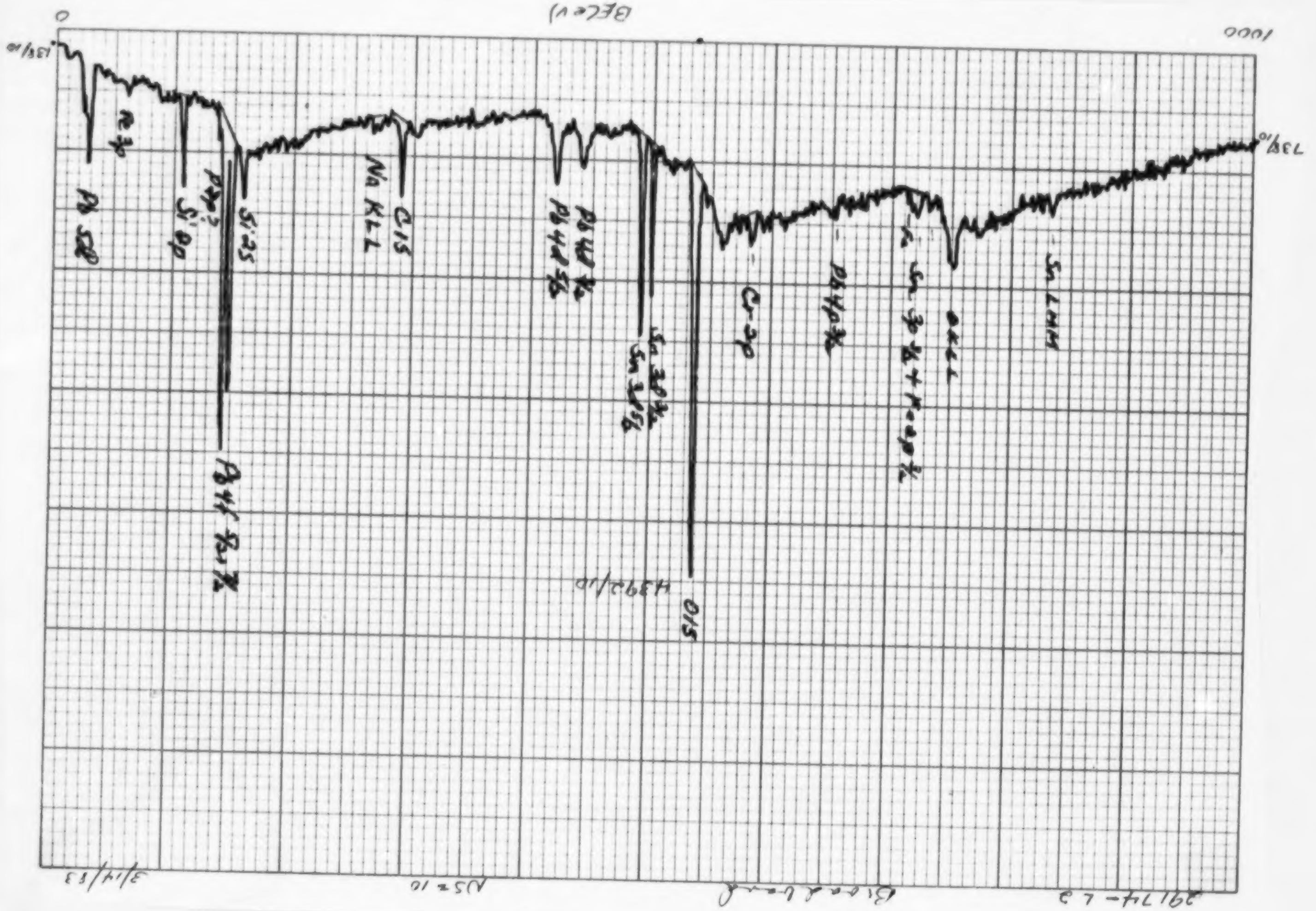
27745-L2 Broadband NS-10 3/15/83




27746-L1
Broadband
NS=10
3/14/83
O1s
6744/10
O KLL
Fe2p1/2
Fe2p3/2
Pb4d3/2
Pb4d5/2
Zn LMM
K2p1/2,3/2
C1s
Zn LMM
Zn LMM
Cl2p
P2s
Si2s
Pb4f5/2,7/2
P2p
Si2p
Zn3p
Fe
Pb+O
727/10
147/10
1000
0
BE(eV)


27746-L2
Broadband
NS=10
3/15/83
C 1s
3136/10
O 1s
Zn LMM
Zn LMM
Zn LMN
P 2s
Si 2s
Pb 4f 5/2,7/2
P 2p
Si 2p
Zn 3p
Sn 3d?
Pb 4d 3/2
Pb 4d 5/2
O KLL
299/10
47/10
1000
0
BE(eV)


29174-L1
Broadband
NS=10
3/7/83
BE(eV)
0
1000
119/10
817/10
4528/10
Pb
Fe 3d
Si 2p
F 2s?
Pb 4f 5/2, 7/2
Si 2s
Cl 2p
Na KLL
C 1s
Ca 2p1/2, 3/2 ?
Pb 4d 3/2
Pb 4d 5/2
Sn 3d 3/2
Sn 3d 5/2
O 1s
Cr 2p
Pb 4p 3/2
Sn
Fe Sn 3p 3/2 + Fe 2p
O KLL
Sn LMM


0
1000
BE(eV)
139/10
738/10
Pb 5d
Re 3p
Si 2p
Pb 5p?
Pb 4f 5/2, 7/2
Si 2s
Na KLL
C 1s
Pb 4d 3/2
Pb 4d 5/2
Sn 3d 3/2
Sn 3d 5/2
O 1s
4392/10
Cr 2p
Pb 4p 3/2
Sn 3p 1/2 + Pb 4p 1/2
O KLL
Sn LMM
29174-L3
Broadband
NS=10
3/14/83